DEVELOPMENT OF A METHODOLOGY FOR MEASUREMENTS AT THE GOBIGAS-GASIFIER

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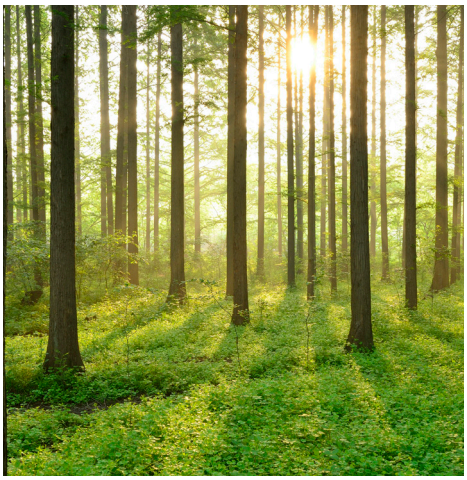

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Development of a Methodology for Measurements at the GoBiGas-gasifier

ANTON LARSSON, HENRIK THUNMAN, MARTIN SEEMANN, CLAES BREITHOLTZ AND INGEMAR GUNNARSSON

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Energiforsk AB | Phone: 08-677 25 30 | E-mail: kontakt@energiforsk.se | www.energiforsk.se

Foreword

This project focus on the methodology for measurements at the GoBiGas Plant. The GoBiGas-plant is based on a process where biomass is converted to biogas using gasification. This type of process is a key technology for decreasing the fossil dependency and an improved methodology for measurements are an important development to commercialize this technology.

The report has been produced by Chalmers University of Technology (CTH), Göteborg Energi AB (GE), Valmet AB (V) and the authors are Anton Larsson (CTH, GE), Henrik Thunman (CHT), Martin Seemann (CHT), Claes Breitholtz (V) and Ingemar Gunnarsson (GE).

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Anton Fagerström (Energiforsk) and Staffan Andersson (GE) are acknowledged for their invaluable help in finalizing the report.

The study had a reference/working group with the following members: Henrik Thunman (CHT), Claes Breitholtz (V), Malin Hedenskog (GE), Anton Larsson (GE), Anton Fagerström (Energiforsk).

Reported here are the results and conclusions from a project in a research program run by Energiforsk. The author / authors are responsible for the content and publication which does not mean that Energiforsk has taken a position.

Sammanfattning

Genom förgasning i en dubbel fluidbäddsförgasare (DFB-förgasare) kan fast och flytande material omvandlas till en energirik gas. Denna gas kan användas för att producera kraft-värme eller, genom syntes, konverters bränsle eller andra produkter. Med målet att producera biometan från skogsrester initierade Göteborg Energi därför GoBiGas-projektet som bygger på denna typ av förgasningsteknik.

I projektet byggdes världens första anläggning för produktion av biometan från biomassa i industriell skala. Första fasen av projektet syftade till att demonstrera tekniken genom att bygga en demonstrationsanläggning med kapaciteten att producera 20 MW biogas. Målet med GoBiGas-projektet är att producera ett andra-generationens biobränsle i form av biometan från restprodukter från skogs- och pappersmassaindustrin, så som grot eller bark. Tekniken möjliggör produktion av biobränslen med en hög hållbarhet och utsläppen av $CO_{2,eq}$, kan reduceras med över 80 procent jämfört med bensin- och diesel, baserat på ”well-to-wheel” analys. Tekniken är därmed en viktig del i omställningen till ett mer fossil oberoende samhälle.

Syftet med projektet var att utveckla metodiken gällande övervakningen och utvärderingen av DFB-förgasare. I detta syfte implementerades ett nytt provtagningssystem vid GoBiGas-förgasaren. Systemet har under projektet används till att genomföra en rad olika mätningar i samarbete med flera andra projekt för att bland annat testa nya mätinstrument, en ny gas reningsteknik, och för att, i detalj utvärdera förgasaren. Baserat på erfarenheten och resultaten från dessa mätningar, ges här en sammanställning av hur metodiken gällande mätningar vid denna typ av process kan förbättras med målet att bidra till utvecklingen av framtida kommersiella förgasare.

En av de viktigaste upptäckterna under projektet var den korrelationen mellan koncentrationen av metan och koncentrationen av tjära i den producerade gasen. Tjäran kan skapa problem nedströms om förgasaren genom att kondensera och därför måste koncentrationen av tjära begränsas. Att mäta tjära är dock komplext och tidskrävande och därför har metoden att kunna bedöma koncentrationen av tjära genom korrelationen med metan varit avgörande för driften av GoBiGas.

Provtagningssystemet som har utvecklats i detta projekt har även möjliggjort att prestandan för förgasaren och gasreningen har kunnat utvärderas i detalj. Mätresultaten har bland annat bidragit till att möjliggöra utvärdering av verkningsgraden för denna typ av process. Undersökningen, som utfördes tillsammans med samarbetande projekt, visar att över 80% verkningsgrad från biomassa till biogas är tekniskt möjligt. Tillsammans med den förbättrade metodiken för att kontrollera gaskvalitén från förgasaren visar detta att tekniken har nått en mognadsgrad som gör att den är redo för kommersialisering. Förgasning har potentialen att spela en viktig roll i framtidens energisystem då den möjliggör konvertering av en rad olika material med en hög verkningsgrad, stabil gaskvalité och låg klimatpåverkan.

Summary

Dual Fluidized Bed (DFB) Gasification is a process where solid or liquid feedstock can be converted into an energy-rich gas. The gas produced can be used for heat and power production, or be synthesized to various fuels or products. Göteborg Energi has built the first industrial-scale plant in the world where biomass is gasified to produce biomethane. The plant it called the GoBiGas-plant and it is a demonstration plant with the purpose of demonstrating the technology and has the capacity of producing 20 MW biomethane. The gasification technology makes it possible to convert biomass into advanced biofuels and the goal of the GoBiGas-project is to use by-products from the forestry industry, such as branches, tops or bark to produce biomethane, to be used as vehicle-gas. The technology enables a high reduction of the emissions of $CO_{2,eq}$, i.e. up to over 80% reduction compared to gasoline and diesel in a well-to-wheel analysis and are an important part of the transition towards a fossil independent energy system.

This project has been focused on developing the methodology for monitoring and evaluation of DFB-gasifiers. For this purpose, a new sampling system has successfully been implemented at the GoBiGas-Gasifier. The system has been used in several collaborations with other projects to test new measurement devices or gas-treatment equipment, as well as for evaluating the gasification process in detail. The methodology regarding measurements at a commercial scale DFB-gasifier has been summarized and discussed in this report with the goal of simplifying the development of future commercial-scale DFB-gasifiers.

One of the most important findings during the project is the correlation between the total yield of tar and the concentration of methane in the gas produced in the gasifier. Tar cause problems in downstream equipment due to fouling, and the level of tar must therefore be limited. To measure tar is both complex and time-consuming and, therefore, the method of monitoring the level of tar using the correlation with the methane concentration has been a crucial development, and the method is successfully implemented to control the gas quality in the GoBiGas-gasifier.

The sampling system developed in current project has also made it possible to evaluate the performance of the gasifier and gas cleaning, and to analyze how the process can be optimized. Measurement results has facilitated the evaluation of the performance in cooperating projects where it has been shown that an efficiency for conversion of biomass to biomethane of over 80% is technically possible. Furthermore, with the improved methodology for monitoring and controlling the gasification developed in this project it has been demonstrated at the GoBiGas-plant that the DFB-gasifiers can be used to produce a gas with a stable gas quality. This shows that the DFB-gasification technology is reaching the technological maturity to be commercialized. Indeed, gasification has the potential to play an important role in the future energy system, enabling a variety of fuels to be converted with high efficiency, with a stable quality of the produced gas, and low climate impact.

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1 Background and Project Aims

Gasification is a technology where solid or liquid compounds are converted into a gaseous mixture, commonly referred to as product gas or synthesis gas. The product gas can be used for a variety of purposes such for combustion, producing heat and power, or be synthesized into products such as methane, diesel or plastics. This makes gasification a key technology for the utilization of carbon-based compounds by enabling the transformation or recovery of carbon-based solids and liquids. By gasifying recovered materials such as waste wood or plastics that no longer can be recycled as material, new products can be produced instead of incinerating these materials improving the circular economy. Further, by utilizing biomass for gasification, bio-based products and advanced biofuels can be produced. Production of advanced biofuels are in-line with the Swedish governments goal of reaching a fossil free vehicle fleet by 2030 [1].

With the aim to produce biogas from biomass using gasification, Göteborg Energi initiated the Gothenburg Biomass Gasification (GoBiGas) project. The first phase of the project included the construction of a demonstration plant for production of 20MW biogas and was cofounded by the Swedish Energy Agency with 222 MSEK. Figure 1 shows a simplified schematic of the GoBiGas-plant where the major components of the process are highlighted. Current project is focused on the gasification and gas cleaning including components 1 to 10 in Fig. 1.

The gasifier at GoBiGas is a dual fluidized bed (DFB) gasifier. The fuel is fed to the bubbling fluidized bed of the gasification reactor (1 in Fig. 1) where it is devolatilized and partially gasified with steam. The unconverted part of the fuel (part of the char) are transported with the bed material to the combustion reactor (2) where it is burnt to generate heat for the process. The combustor is a circulating fluidized bed and the particles are separated from the flue gases using a cyclone (3). In this way heat can be transported between the reactors by circulating the bed material without mixing the gases generated in the two reactors. Thereby it is possible to produce an energy rich gas, referred to as product gas, with very low concentrations of nitrogen, making it suitable for synthesis. It is also for this purpose that the fuel is fed *via* lock hoppers (10) where air is removed.

To sustain the temperature of the process, part of the product gas is burnt in the combustor in addition to the char. Some product gas may also be burnt in the post combustion chamber (4) that is used for destruction of various low calorific off-gases from the synthesis part of the plant. The flue gases are cooled and cleaned in the flue gas train (9). The product gas is conditioned in several steps, first step is the product gas cooler (5) where the gas is cooled to between 160-230°C. Then particles are removed in a textile bag filters (6, referred to as the product gas filter) before scrubbing the gas with rape-methyl-ester RME (7) to remove tar. Remaining tar components are removed using adsorption beds with activated carbon (8). In remaining process steps (11-19) the gas is treated and upgraded to biomethane that is fed to the natural gas grid. The process is described in further detail here [2].

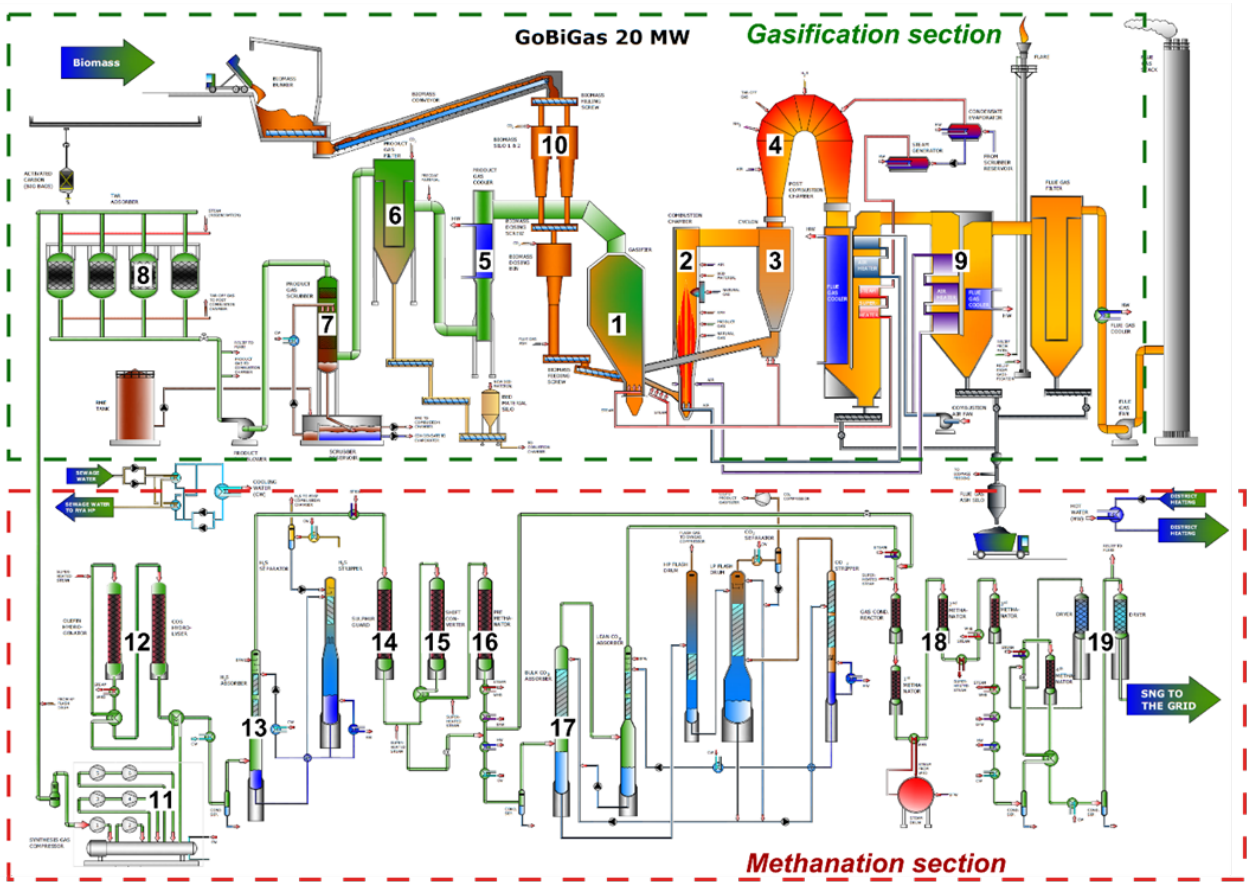


Figure 1: A Schematic overview of the GoBiGas-plant including a list of the major process steps.

The purpose of this project was to establish a new sampling system to enable measurements and tests with new equipment at GoBiGas and to improve the evaluation of the GoBiGas process; facilitate tests with new equipment; and to develop the methodology for measurements at industrial scale DFB gasifiers. A number of measurable aims were established in relation to the project purpose:

- Aim 1: To increase the scientific level of the evaluation of the GoBiGas-plant, a method should be established to quantify the carbon conversion in the gasifier as well as the yield of undesired organic compounds, such as tar.
- Aim 2: To establish a sampling system that enables the sampling of the gas produced in the gasifier for analysis in at least 2 parallel measurement systems, yielding complementing information.
- Aim 3: Investigate the performance of the new sampling system regarding tar and gas measurements.
- Aim 4: Arrange measurements with collaborating projects using the new sampling system to demonstrate new measurement techniques or gas conditioning equipment. In line with this aim at least 2 relevant measurement campaigns should be performed in cooperation with other projects.

2 Experimental

Since the start of this project, 2015-02-01, the GoBiGas-gasifier has been operated for more than 7500 hours (>11 000 hours total) and the availability are illustrated in Fig. 2. Each green bar represents the length of each operational period and the blue line represents the accumulated time of operation. During this period of time there has been several challenges that has affected the availability of the process, also affecting the focus of some of the measurements conducted during current project.

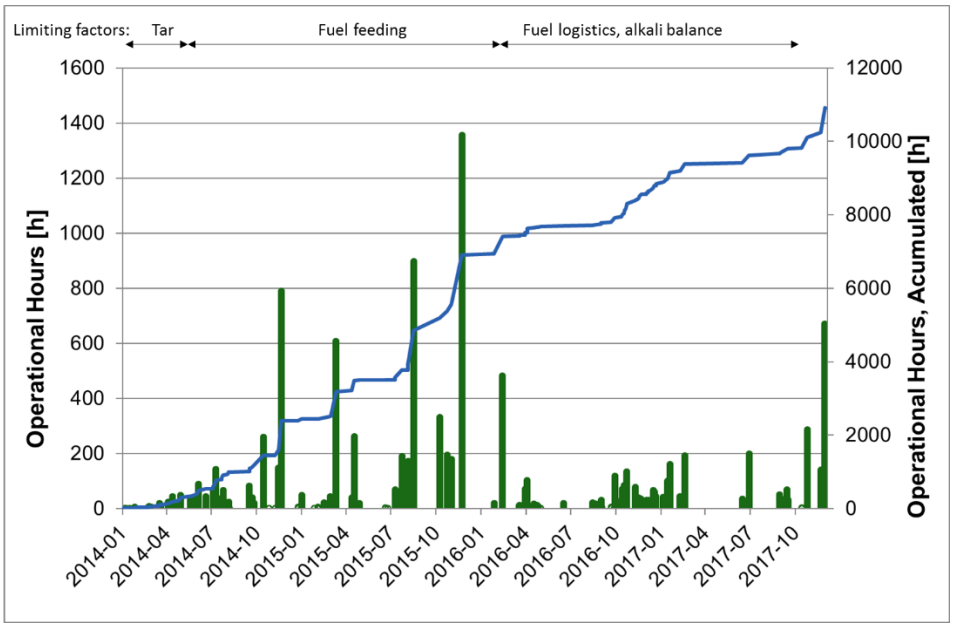


Figure 2. Availability and major limiting factor of the GoBiGas-Gasifier.

The first gasification was performed by the end of 2013 and the plant was initially operated using wood pellets as fuel. The limiting factor for the operation was initially related to the high level of tar in the product gas, which caused clogging of the product gas cooler in just a couple of hours. In March 2014 a major breakthrough was made concerning the tar yield when potassium was added to the process. This reduced the yield of tar significantly and enabled continuous operation without major clogging of the product gas cooler. The approach of adding potassium was based on results from the pilot gasifier at Chalmers University of Technology, referred to as the Chalmers-gasifier, see Marinkovic *et al.* [3]. By pumping the potassium in the form of K_2CO_3 solved in water to the combustion side of the process, "activation" of the bed material was achieved. Numerus papers has been focused on the activation of bed material to improve the gasification and reduce the tar yield from DFB gasifiers, e.g [3-6]. However, there are still no consensus regarding the mechanism during the activation, and in what manner it affects the tar yield. Here, the term activation of the bed material, or level of activation is used to refer to the bed materials ability to limit the tar yield. This project focus on how to monitor and control the level of activation of the bed material rather than describing its mechanism. Measurements were conducted to

establish correlations between the permanent gas components (that is relatively easy to measure) and the total yield of tar (that is more challenging to measure). Furthermore, online measurements of tar and alkali concentrations in the product gas was carried out to learn how to monitor and control the activation level of the bed material.

With the yield of tar under control the major limiting factor for the availability of the GoBiGas-gasifier was the fuel feeding, while the major limiting factor for the load was the adsorbent beds of activated carbon (8 in Fig. 1). The activated carbon is used to clean the gas from light aromatic compounds (mainly Benzene, Toluene and Naphthalene) which could not be captured by the RME-scrubber, and thereby protect downstream catalyst that could otherwise suffer deactivation.

In the spring of 2016 a new fuel storage and feeding system was installed to enable operation with chipped or crushed fuel as alternative to the pelletized wood used during the startup. Switching fuel caused additional availability problems mostly related to mechanical problems with feeding the biomass, as well as too high moisture content in the fuel. Changing the fuel, also affects the activation of the bed material and the correlations between the permanent gas and tar, thus further measurements were conducted to enable monitoring and control of the activation of the bed material using different fuels.

In addition to the measurements used to control and monitor the process as mentioned above, one aim of the project was to increase the availability of the GoBiGas-gasifier for cooperating research projects, and enable measurements for the evaluation of the performance of the process using the mass and energy balance.

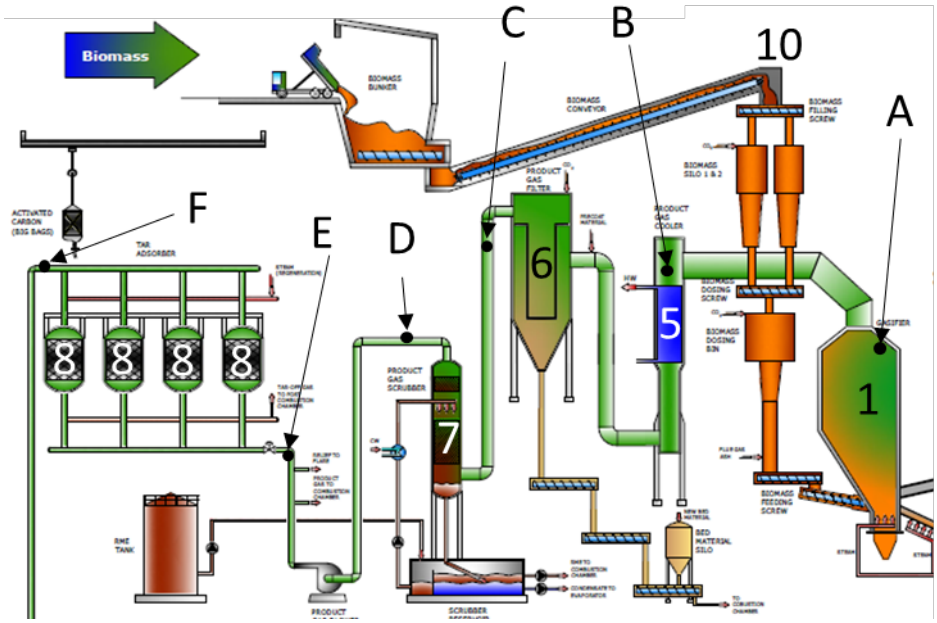


Figure 3. Indication of the main measurement positions: A) Freeboard of the Gasifier; B) Before the product gas cooler; C) After the product gas filter; D) After the RME-scrubber; E) online product gas analyzer (reference); and F) After the adsorption beds of activated carbon, related to the process steps: 10) fuel feed; 1) Gasifier; 5) Product gas cooler; 6) Product gas filter; 7) RME-scrubber; 8) adsorption beds of activated carbon.

The measurement positions used in this project are illustrated in Fig. 3 and they were selected to enable evaluation of the different process steps of the product gas cleaning, as well as the gasifier. In general, more information about the gasifier can be received, the closer to the gasifier one measure, but it also becomes more challenging, the closer to the gasifier one tries to measure. Thus, there is a tradeoff between the complexity of measurements and the information that can be received, that should be considered when developing the methodology for measurements at a commercial DFB-gasification plant.

2.1 NEW SAMPLING SYSTEM

To enable continuous measurements at points B-D, a new gas sampling system was developed and installed at GoBiGas. The sampling system should simplify testing of new instruments or equipment and enable switching between sampling from either point B, C or D without moving the equipment. The location for the sampling system was chosen so that safety requirements could be fulfilled, and so that auxiliary systems can easily be accessed, including pressurized air, cooling water, purge gas, ex-classed electricity connections (1 and 3 phase), and grounding. The position is located away from any ex-zones and for further safety the electrical supply is connected to the gas detectors in the plant so that, in case of a gas leakage, all experimental equipment will automatically shut down.

To minimize the risk of gas leakages from the sampling system itself and the equipment connected to it, the system was outlined to always work at sub-pressure. This is possible by sampling the gas from locations in the system that is operated at a slight sub pressure and by feeding the off-gases for combustion in the PCC, which is operated at even lower sub-pressure. The sub-pressures are controlled by the product- and flue-gas fan respectively. The process scheme (P&ID) of the new sampling system are shown in Figure 4. In addition to gas from the three sampling positions B-D, purge gas (N_2) can be feed to the system through a rotameter to flush the system during startup and shutdown or to pulse the filter used for sampling gas from position B.

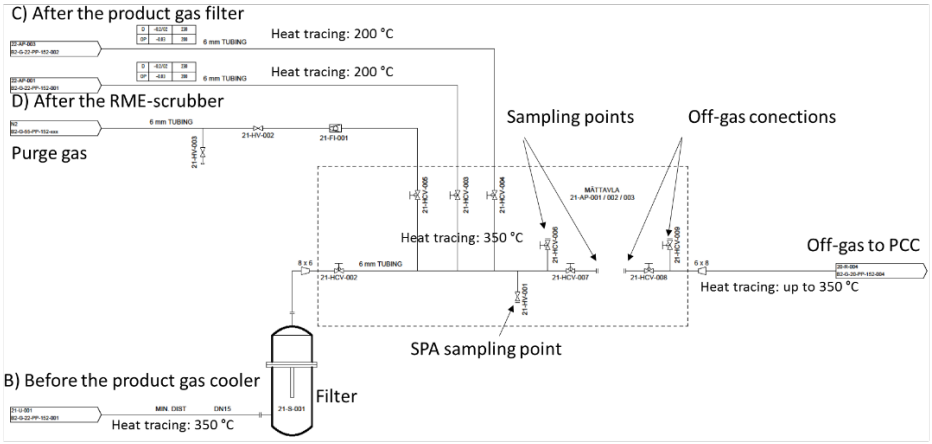


Figure 4: Schematic overview of the sampling system based on the P&ID. Sampling points B-D corresponds to the sampling points in Fig. 3.

Figure 5 shows a picture of the sampling panel where equipment or measurement devices are connected. The heated hoses and regulators used to transport the gas from the sampling probes to the sampling board are from Hillesheim GmbH and heat the gas sampled from point B to 350 °C and the gas sampled from points C and D to 200 °C to avoid condensation of tar in the sampling lines. The sampling panel as well as the filter house are heated to 350 °C using heating cables from ISOHeat (MiL-HT-BS30) and the valves are high temperature needle valves from Swagelok (SS-3NBS6MM-G-SE6-SH). A syringe is used for the SPA sampling, further described below, and to get the needle into the flow of sampled gas in a good way a ball valve (SS-S62PS6MM-EK4) was installed prior to the septa. This also allows one to change the septa during operation, which is required as it is penetrated with the needle to reach the sampling gas and eventually starts leaking air into the sampling gas, disruption the measurements.

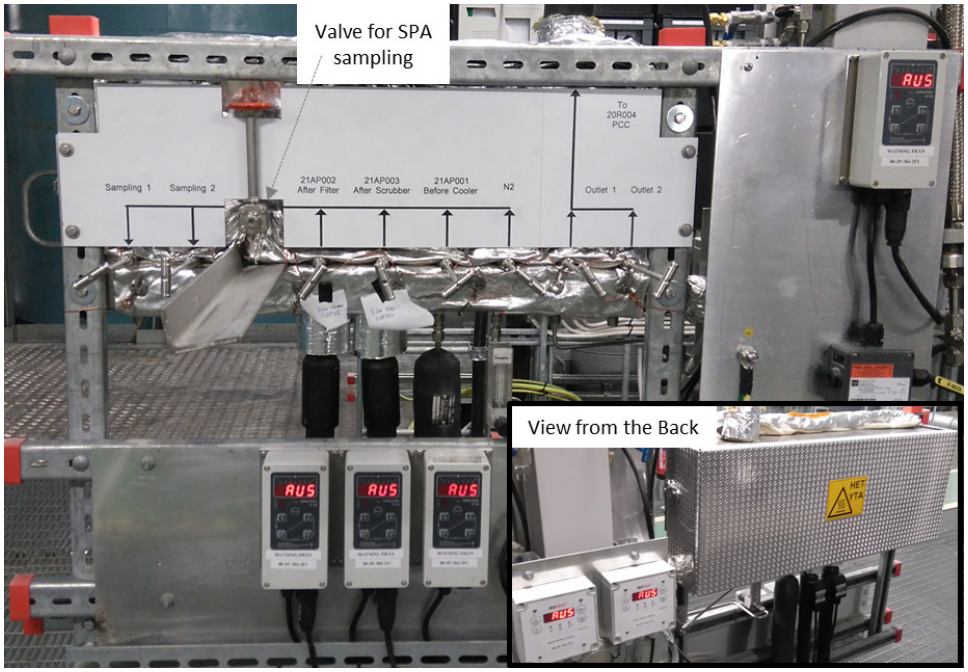


Figure 5: Picture of the new sampling board with all the valves, connections and temperature controllers. Everything can be heated to 350 °C and corresponds to the area indicated with a dotted line in Fig. 4.

As mentioned, the closer to the gasifier the more complex it becomes to sample the gas as the gas from the gasifier is hot and contain tar, particles as well as gas phase ash components, e.g. alkali components. However, to get an accurate analysis of the tar, gas must be sampled prior to the product gas cooler as some tar components are removed in the product gas filter or even get stuck in the cooler. To cope with the challenging environment in the product gas line before the cooler, where the temperature is typically in the range of 650-850 °C, a temperature-controlled sampling probe was designed. To avoid significant condensation of tar components, the temperature should be kept above 300 °C while to remove the alkali salts the temperature should be reduced below about 350 °C. Further, the material in the probe should be cooled to avoid mechanical stress on the material

when the temperature of the product gas is high. DFB-gasifiers are fluidized with steam which is superheated to improve the efficiency of the process, which means that a suitable cooling media in terms of the superheated steam are available. Another advantage with using steam is that it can be vented straight into the product gas which significantly simplifies the design of the probe, as to compare with e.g. a thermal oil system.

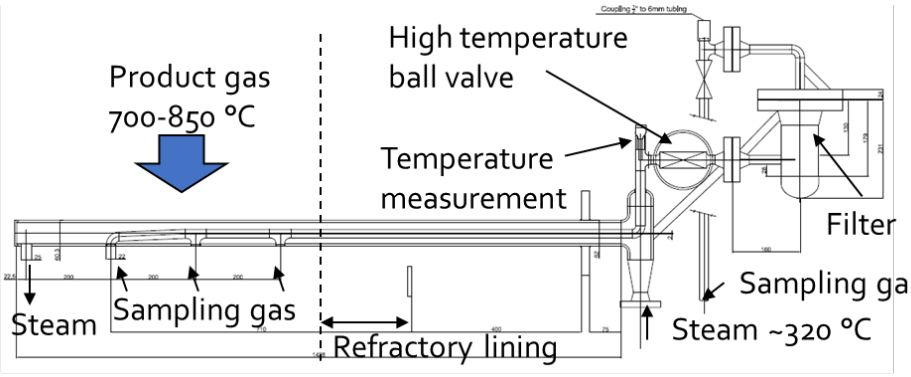


Figure 6: Cross-section of the sampling probe at sampling point B (Fig. 3 and 4)

Figure 6 show the cross-section of the sampling probe that was designed as a fixed installation with an outer casing for the steam and an inner tube for the sampling gas. To reduce the risk of measurement errors due to poor mixture, the gas is sampled from three points along the radius of the product gas line; at the center, 10 cm from the edge, and one in the middle these two. The temperature of the sampled gas is measured and can be controlled by adjusting the steam flow. The sections that are not temperature controlled using steam, are instead heated with electricity and are well insulated to avoid cold spots. To enable safe service of the filter during operation of the gasifier a high temperature ball vale that can cope with temperatures over 500 °C was welded in prior to the flange connecting the probe and the filter. The gaskets for the flanges is made of graphite that can cope with the elevated temperatures. The filter is a CERAFIL XS-650, which is a ceramic filter that can cope with the temperature and remove both soot and alkali particles if a suitable gas velocity can be attained through the filter, see the producer's specification. Present setup was designed to cope with a volume flow of up to approximately 10l_n/min and the length of the filter was adjusted to the minimum length required for this volume flow to minimize the size of the filter house, see Fig. 7.

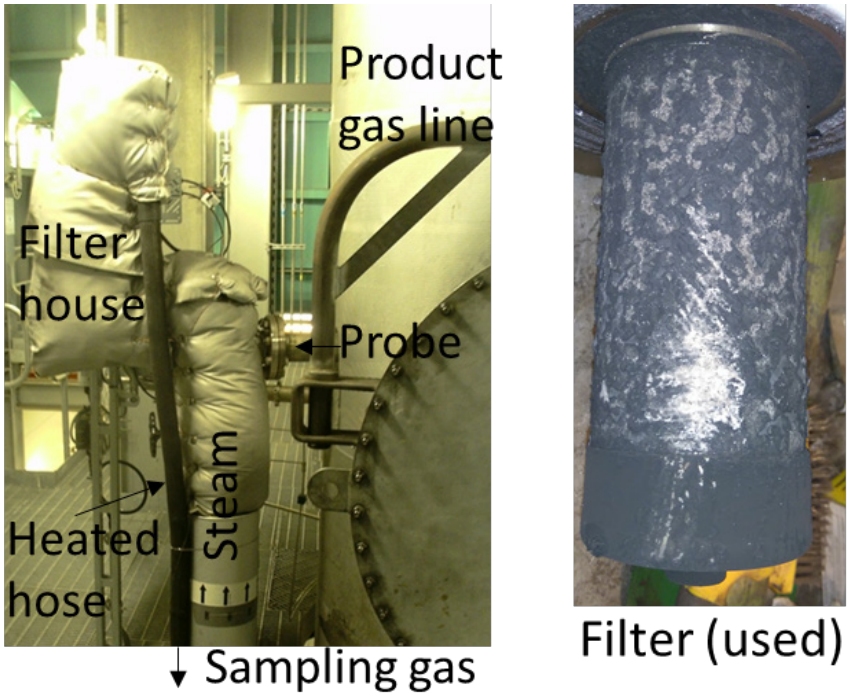


Figure 7. Sampling system as installed on-site at GoBiGas in the product gas line just prior to the product gas cooler (left) and the filter fitted inside the filter house (right).

The outer shell of the probe was constructed using alloy INCOLOY 800HT (material nr. 1.4876) that can cope with temperatures, avoiding damage if the steam cooling would be out of operation. The rest of the system is constructed in stainless steel (material nr. 1.4432). As there are a lot of particles in the product gas, attrition of the probe is a potential problem and protective coating was therefore applied. The environment in the product gas line are severe with elevated temperature, a reducing atmosphere, lots of particles, and a high concentration of alkali compounds, and it was unclear how classical high temperature coatings would cope with this environment. Therefore, a cooperation with Surftech Engineering AB was initiated to test out two different coating materials in this environment. Figure 8 shows how the two coatings of ZrO_2 (100%) and Al_2O_3 (97 % Al_2O_3 and 3 % TiO_2) was applied to the probe. Part of the probe was left uncoated and a space of uncoated material was left in-between the coatings to enable investigation of how the edges of the coating material can cope with the environment.

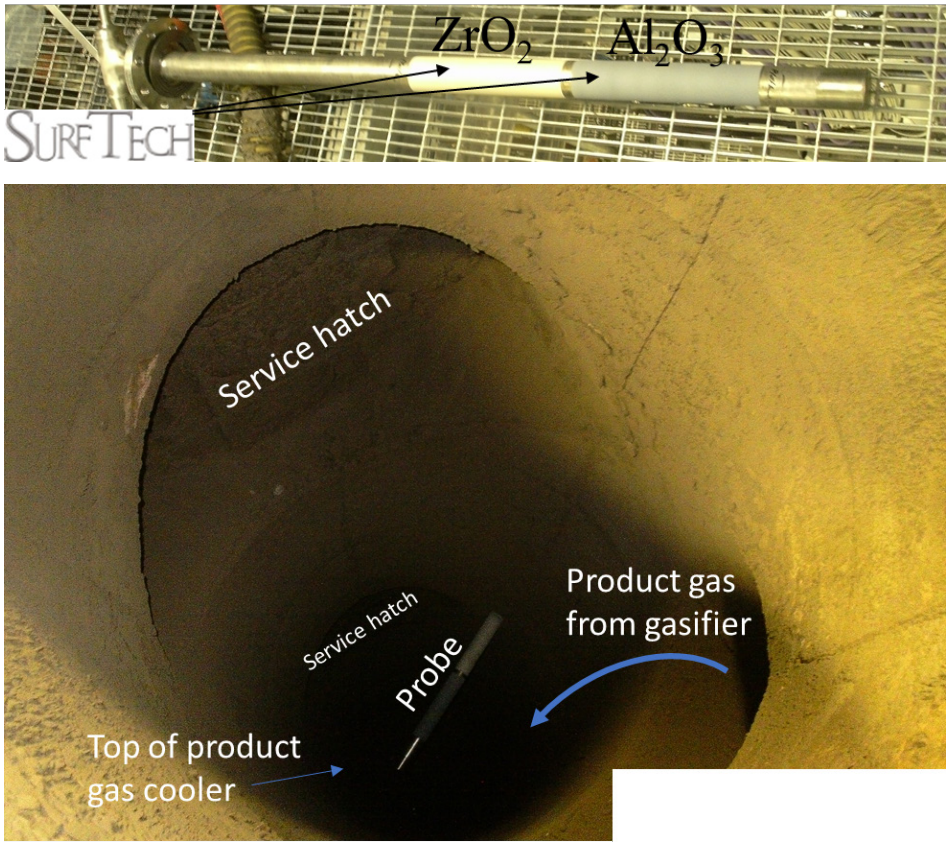


Figure 8: Picture of the sampling probe and the coatings applied by Surftech (upper) and a picture of the probe in the product gas line (DN1000) viewed from above (lower).

The sampling system has so far been operated for more than 500 h with satisfying functionality. Some initial challenges regarding the tracing of the filter house and connection to the heated hose had to be fixed by adding additional regulators (one for each tracing element) and carefully placing the thermocouples so that the regulators receive representative temperature readings.

2.2 MEASURMENTS

A range of measurements has been conducted during the course of this project and these are described below where they are sorted after the scope of the measurements:

- Particles and alkali compounds
- Benzene, Toluene, and Xylene (BTX) and tar components
- Permanent gas components

2.2.1 Particles and Alkali Compounds

The particles and alkali compounds has been investigated using both online measurement and by analysis of deposits of the inlet of the product gas cooler.

Online measurements of particles and alkali concentrations were conducted in a collaboration with the University of Gothenburg and the research institute RISE as part of a collaborating project. A project report are available in Swedish[7] but results has also been published as scientific paper in English [8] where the system is described in detail. Briefly, the system utilizes a specialized sampling probe and dilution chamber to cool and dilute the gas so that alkali components are in solid phase that can be measured with a Surface Ionization Detector (SID).

If too much potassium is feed to the process, deposits starts forming on the inlet of the product gas cooler, leading to an increase in the pressure drop over the cooler eventually forcing a stop of the process. The deposits were sampled and analyzed with X-ray diffraction XRD.

2.2.2 BTX and Tar Components

BTX and other tar components are important to measure to evaluate the fuel conversion in the gasifier but also to evaluate and control the downstream gas cleaning steps. The concentration of tar in the product gas has been analyzed using two methods:

- Offline measurements using solid phase adsorption (SPA)
- Online measurements with prototype equipment, CON-TAR.

The SPA method has previously been described in detail [9, 10] and the sampling was thoroughly evaluated based on measurements at the Chalmers-gasifier[10]. Briefly, the method is based on the extraction of a known amount of product gas through an adsorbent where the tar components are adsorbed. 100ml gas is extracted into a syringe using a pneumatic robot to have a consistent pull during the sampling. The tar components adsorbed are later dissolved, using dicloromethane (DCM) and then analyzed together with a trace component (4-etoxyphenol) in a GC with a flame ionization detector (FID). The GC-FID has been calibrated with 30 different components at 3 different concentrations. The known components correspond to the major part of the tar and can be quantified with a high accuracy. Unknown components are also detected and can be quantified, but with an unknown response factor, so the accuracy is slightly lower. With a quantified amount of the trace component in the solvent, the tar levels can be related to the gas volume in the syringe. By also compensating for the temperature of the gas in the syringe, as well as the moisture content in the gas (saturation concentration based on temperature) the concentration of tar in the dry part of the product gas during normal condition (Pressure = 101325 Pa, Temperature = 273,15 K) can be calculated and be presented as g/m_n^3.

Depending on the main components of interest, the temperature, and steam content of the gas, different adsorbents can be used. Two types of adsorbents have been used at GoBiGas both bought from Sigma-Aldrich, one with an amine adsorbent (PK54 SUPELCLEAN LC-NH2), and one with both an amine and an adsorbent based on activated carbon (Supelclean™ ENVI-Carb/NH2 SPE Tube), see Israelsson *et al*. [10] for more details.

When samples are taken from a hot gas stream (300-350 °C) with high steam content (30-50%), such as gas sampled from point B in Fig. 3, the amine will be

significantly heated during the sampling by the thermal energy in the gas and condensation of steam. This decreases the amines ability to adsorbed lighter components, such as BTX components, and for an accurate measurement of these compounds the adsorbent with additional activated carbon should be used. However, if the focus is to measure low tar concentrations in a gas stream with low moisture content and temperature (below 100 °C), such as the gas downstream of the beds with activated carbon (point F in Fig. 3) it might be better to use the adsorbent without activated carbon. When measuring low concentrations, it is important to clean the adsorbent prior to sampling to remove impurities and this is much more convenient with only the amine in place as the cleaning process will affect the carbon part in a negative manner.

In general, the adsorbent with both amine and activated carbon are used when sampling from position B and C (see Fig. 3) and the adsorbent with only an amine are used for sampling from position D and F. During the project more than 140 measurements using SPA has been conducted. For each measurement, 4-6 adsorbents are used for sampling in series and evaluated separately and the average value of all successful samplings are used as result. Each sampling and dissolving takes about 1 hour and the following analysis in the GC-FID takes about 2 hours for each adsorbent. With the final evaluation of the GC-data, this means that the results can be ready several hours or even the day after sampling. The method also requires an on-site lab where the samples can be dissolved, conveniently also equipped with a GC to conduct the analysis as well. The benefit of the SPA-method is a safe and convenient sampling, appropriate for a commercial process with strict safety regulations and that it gives an accurate quantification of specific tar components.

Another commonly applied method for measuring tar is the *tar protocol* [11] and this was considered as an alternative for the SPA-method. However, this method involves the use of glass impingers containing combustible and hazardous liquids and this is something that, from a safety and health perspective, should be avoided. Further with the SPA method the tar is sampled for 1 minute as compared to about 20 min for the tar protocol, and better time resolved measurement can be done with the SPA method. This is important to detect if there are concentration peaks. Based on these features, Göteborg Energi deemed the SPA-method to be the most appropriate method for measuring tar at GoBiGas.

In addition to the new sampling system, an alternative sampling approach for the SPA method was applied at sampling position B. With this method, samples are extracted directly from the product gas line using a long and narrow (6 mm diameter) probe that can be inserted in the process during operation. In a similar manner as for the regular SPA method described above gas is extracted through the adsorbent but in this case, some of the tar will condense in the probe. The volume in the probe are initially just air and must be subtracted from the volume of gas extracted with the syringe. To decrease the uncertainties related to the sampling, 4 absorbents are used in series while keeping the probe in place and each time condensing some of the tar in the probe. The probe is cleaned with DCM to evaluate the amount of tar in the probe in addition to the tar adsorbed by the amines.

The benefit with the probe-based method is that no elaborate continuous sampling system is required. However, the sampling procedure is more complex requiring 2 people for 2 hours to take the sample and 2 people 2 hours to prepare the sample for GC analysis. In addition, the probe approach requires that a valve to the process must be opened to insert the probe, which is always a moment of some risk that should be minimized in a commercial application.

Online measurement of tar

In cooperation with a EU-project (an Eranet BESTF project) called BioProGReSs an online analysis instrument, developed at TU Berlin and called CON-TAR, was connected to the new sampling system at GoBiGas. The equipment is described in detail elsewhere [12, 13]. In summary, the technique is based on light induced florescence (LIF), by using a light emitting diode (LED) that exhibits ultra violet (UV) light through an optical window into the sampling line. The properties of the poly-aromatic compounds make them appropriate to excite with the UV-light, which enables analysis of the resulting fluorescence light from these compounds. The analysis gives an on-line qualitative measurement of the total level of tar, in this case Naphthalene and larger components, in the product gas. With calibration, it could also be used for quantification.

The gas flow though CON-TAR is created with a built-in jet pump and the gas is combusted in a catalytic oxidizer after the measurement cell to avoid downstream clogging, both steps requiring pressurized air. The optical window is purged with nitrogen to avoid condensation, thus requiring nitrogen (1 l/min) to run properly. Further, the LED requires continuous cooling and cooling water of about 20 °C where used. The setup also has a built-in lambda-probe that gives an indication when gas is properly sampled and not. The prototype has been convenient to operate in connection to the new sampling system and has been operated around the clock, measuring the tar level in the gas in point B, C or D for a total of more than 400 hours.

2.2.3 Permanent Gases

- The permanent gas composition has been measured with two methods:
- The ordinary product gas analyzer at GoBiGas;
- and a mobile μGC

The GoBiGas plant was equipped with an online product gas analyzer built by ABB AB and that samples gas from point E (Fig. 3), after the RME-scrubber. The sampling line is heat-traced to keep about 60 °C to avoid clogging and the analysis cabinet is equipped with an additional small RME-scrubber and cooler to condition the gas. The components measured online are H_2, CO, CO_2, CH_4 and O_2. The measurement techniques and calibration levels are summarized in Table 1.

Table 1. summary regarding the components analyzed with the ordinary product gas analyzer at GoBiGas.

Component	Measurement technique	Calibration levels (%Vol)	Comments
H_2	Thermal conductivity detector (TCD)	42	
CO	Non-dispersive infrared sensor (NDIR)	23	
CO_2	NDIR	24	
CH_4	NDIR	12	
O_2	Magnetomechanical oxygen analyzer		2 parallel instruments as part of the safety system.

The product gas from the gasifier contains more component than can be measured with the ordinary product gas analyzer. Therefore, a mobile μGC has been used extensively for more than 300 hours during the project, to measure the concentrations of permanent gas components as well as Benzene. The μGC is an Agilent 490 with 3 installed columns with individual thermal conductivity detectors (TCD). The calibration levels and the linearization used for the calibration curves are summarized in Table 2.

Table 2: summary of components analyzed with the μGC and the calibration used.

Component	Column type/ support gas	Calibration levels ($\%_{vol}$)	linearization/ including zero	Comments
H_2	COX/Argon	15.112, 28.74, 40, 50.05	Linear, no	
CO	COX/Argon	7.995, 19.366, 25, 39.428	Linear, no	
CO_2	PPU/Helium	4.998, 8, 15.06, 21, 27.198	Quadratic, no	
CH_4	COX/Argon	8.02, 9.994, 16.009	Linear, no	
Air (N_2, O_2)	COX/Argon	3.021, 4.43, 7.814	Linear, yes	Not separated
He	COX/Argon	0.05, 0.20	Linear, no	
C_2H_2	PPU/Helium	0.2498, 0.4991, 1.001	Linear, yes	
C_2H_4	PPU/Helium	0.5, 1.5, 2.001, 5.003	Linear, no	
C_2H_6	PPU/Helium	0.2005, 0.5084	Linear, yes	
C_3H_x	PPU/Helium	0.2006, 0.4984, 0.7011	Linear, yes	C_3H_6 and C_3H_8 Not separated
H_2S	PPU/Helium	0.1002, 0.503	Linear, yes	
SO_2	PPU/Helium	-	-	Only qualitative
C_6H_6	Wax/Helium	10ppm	Linear, yes	
C_7H_8	Wax/Helium	-	-	Only qualitative
C_3H_8O	Wax/Helium	-	-	Only qualitative Scrubbing liquid
H_2O	Wax/Helium	-	-	Only qualitative

The method used for the different columns are summarized in table 3. The method has been tuned to enable measurements of very low concentrations of He and to

give a sufficient separation between the different components. Separation of the major components in air (N_2 and O_2) was not possible with current column. This could be achieved by using a PPQ column instead, but this column is more sensitive to water and therefore, needs to be regenerated and recalibrated more often and it is therefore not suitable for present purposes.

Table 3:

Column	Injector temp. (°C)	Column temp. (°C)	Pressure (kPa)	Analysis time (S)	Injection time (mS)	Backflush time (s)
1	80	80	130	180	40	8.5
2	65	65	130	180	40	30
3	110	70	100	180	40	-

The mobile μGC setup is equipped with a membrane pump to generate a continues gas flow that the GC can sample from, Fig. 9. The gas flow is cooled to about 5 °C to minimize the water content of the gas, and, dependent on the sampling point, the gas is scrubbed with isopropanol to protect the GC from tar components that could clog the sampling line and damage the GC. The maximum regeneration temperature with the current column setup is 170 °C and components that cannot be flushed out at this temperature will remain in the columns, permanently disturbing the measurements. With the isopropanol scrubber and the cooler, no such disturbance has been detected.

The isopropanol scrubber has been used for measurements at all sampling points except when sampling the gas after the adsorption beds (point F) where the gas is clean enough to analyze without the scrubbing. When using the scrubber some components, such as Benzene and H_2S, will be dissolved in the condensate (isopropanol and water from the gas). However, the scrubber liquid is circulated and can, therefore, be saturated after a certain amount of time. This time is dependent on the components solubility in the liquid and the concentration in the gas. For some components like, CO_2, it is quick enough, not to disturb the measurements, while for H_2S it is slow and in best case a rough average of the H_2S concentration can be estimated from the measurements when using the scrubber.

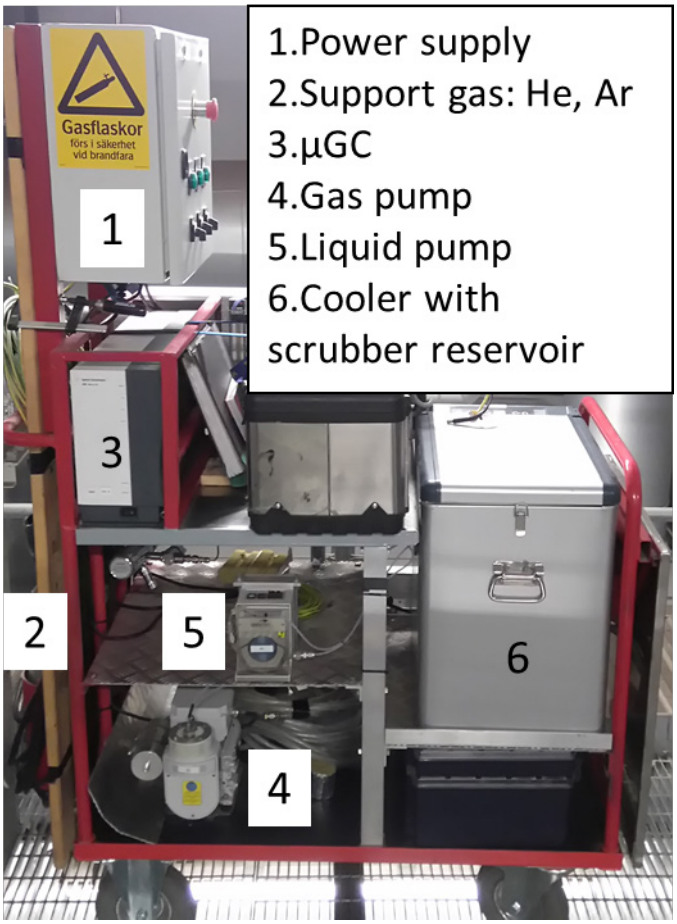


Figure 9: The mobile µGC used for measurements at GoBiGas.

2.3 CONTROL PARAMETERS

It is important to minimize the complexity of measurements required at a commercial scaled gasifier and extract as much information as possible from the ordinary gas analysis. For this purpose, an investigation has been conducted to find correlations between the tar level in the gas and the concentrations of CH_4, H_2, CO and CO_2 that are easy to measure with high time resolution. Two parameters have been found particularly useful for monitoring and controlling the GoBiGas process:

- CH_4 concentration
- Syngas modulus

A crucial development for the GoBiGas was the formulation of a methodology for how to control the activation of the bed material and, thereby the yield of tar based on the concentration of a component measured with the online analyzer. Linear regressions were established between the total tar measured *via* the SPA method, and the concentrations of the different gas components where the CH_4 concentration were found to be strongly correlated with the total yield of tar.

The syngas modulus was defined based on the concentration of the components of a pure syngas, H_2, CO and CO_2. By studying the H/C-ratio and O/C-ratio based on

these components in a specialized Van Krevelen diagram [14] one can qualitatively evaluate the fuel conversion in the gasifier based on these standard online instruments. Figure 10 shows an example on how the operation of GoBiGas-gasifier with an activated bed material can be compared to operation without proper activation. The different operational cases from GoBiGas is also compared to the gas measured from a lab-scale bubbling fluidized bed pyrolyzer used as a reference point. The ratios based on the syngas components of the pyrolysis gas are summarized together with the ratios of the dry ash free fuel in Table 4.

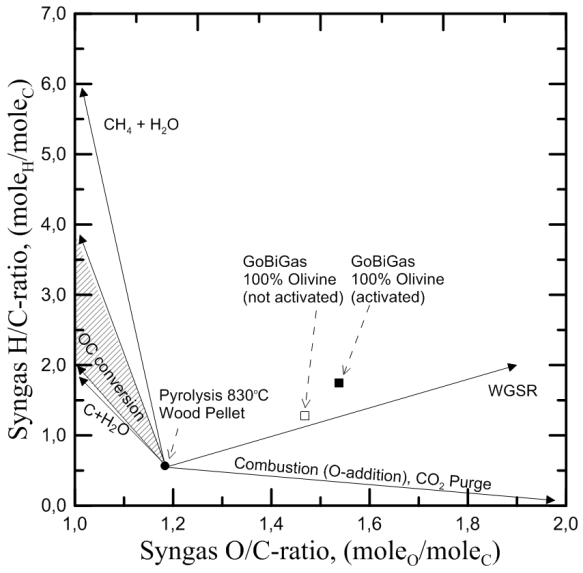


Figure 10: A specialized Van Krevelen diagram illustrating the reaction vector, reference composition based on pyrolysis and two examples of gas from GoBiGas.

Table 4: Molar ratio of the main components in the dry ash free fuel and pyrolysis gas respectively.

	H/C	O/C
Dry ash free fuel	1.452	0.638
Pyrolysis gas (H_2, CO, CO_2)	0.589	1.185

A set of the major global reactions occurring in the gasifier can be used to visualize the fuel conversion, indicated as vectors emanating from the pyrolys case in the direction in which the reaction affects the syngas composition. The reactions, *R1-R8*, are summarized in Table 5 where the water gas shift reaction (WGSR), *R8*, are unique in the sense that it adds or removes hydrogen and oxygen with a fixed ratio without affecting the amount of carbon in the syngas. This means that the WGSR vector has a fixed direction that is independent on the starting coordinate in the diagram. The other reactions, *R1-R7*, instead has a fixed end-point meaning that the direction of the vector will change depending on the starting point. This makes the WGSR vector a useful reference line where additional fuel conversion through reactions *R3-R7* is required to have a coordinate above the WGSR based on the reference pyrolysis case. To have a coordinate below the WGSR-line, combustion of part of the fuel, *R1-R2*, is instead required. By plotting the syngas composition like this, different operational case or even different reactors can be qualitatively

compared even without a complete mass-balance and without the need of complex and time-consuming tar analysis. With a good measurement of the gas flow a quantitative analysis could even be made and this has been described in more details in previously publications[15, 16].

In Fig. 10 one can spot that when operating without an activated bed material the coordinate for the syngas is close to the WGSR line of the pyrolysis case. This indicates little conversion of char and hydrocarbons such as CH_4 or larger organic compounds (OC) such as tar. For the activated case one can see that the WGSR has been further promoted, but additional conversion of other components into syngas has also occurred as indicated by a larger distance to the reference WGSR-line. Although the graphical approach is useful for evaluating the fuel conversion in a gasifier it is more convenient to define a single parameter to evaluate the process online.

Table 5: Summary of the major global reactions used to describe the fuel conversion in the gasifier

Description	Reaction	Ref.
Char combustion	$C(s) + O_2 \rightarrow CO_2$	R1
Volatile combustion	$C_z H_v O_w + \left(z + \frac{v}{2} - w\right) O_2 \rightarrow (z)CO_2 + (v/2)H_2O$	R2
Char gasification	$C(s) + CO_2 \rightarrow 2CO$	R3
Char gasification	$C(s) + H_2O \rightarrow CO + H_2$	R4
Reformation of tar components	$Tar + \alpha_1 H_2O + \alpha_2 CO_2 \rightarrow \alpha_3 Tar^* + \alpha_4 C_x H_y + \alpha_5 CH_4 + \alpha_6 CO + \alpha_7 H_2 + \alpha_8 C(s) + \alpha_9 CO_2$	R5
Reformation of light hydrocarbons	$C_x H_y + xH_2O \rightarrow xCO + \left(\frac{x}{2} + y\right) H_2$	R6
Methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	R7
Water gas shift reaction (WGSR)	$CO + H_2O \leftrightarrow CO_2 + H_2$	R8

The syngas modulus, Ψ, is defined to describe how well the fuel is converted into a pure syngas of H_2, CO and CO_2, where a value of 1 corresponds to complete conversion into syngas and 0 corresponds to the reference pyrolysis case. Ψ, corresponds to the fraction of perpendicular distance from the WGSR-lines based on the pyrolysis case to the measured case compared to the theoretical case of complete conversion of the fuel, as summarized in Table 6 and illustrated in Fig. 11.

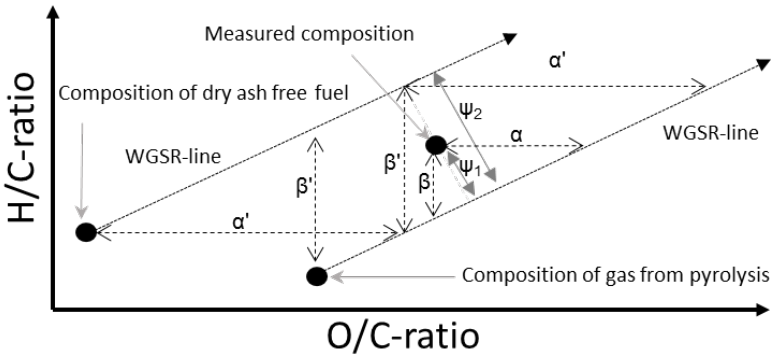


Figure 11: Illustration of the parameters used for the calculation of the syngas modulus, which are summarized in Table 6.

Table 6: Summary of equations for the calculations of the syngas modulus.

Syngas modulus: $\Psi = \Psi_1 / \Psi_2$
$\Psi_1 = \frac{\alpha\beta}{\sqrt{\alpha^2 + \beta^2}}$
$\Psi_2 = \frac{\alpha'\beta'}{\sqrt{\alpha'^2 + \beta'^2}}$
$\alpha = \left(^{O}/_{C}\right)_{pyro} - \left(^{O}/_{C}\right)_{measured} + \left(\frac{\left(^{H}/_{C}\right)_{measured} - \left(^{H}/_{C}\right)_{pyro}}{2}\right)$
$\beta = \left(^{H}/_{C}\right)_{measured} - \left(^{H}/_{C}\right)_{pyro} - 2\left(\left(^{O}/_{C}\right)_{measured} - \left(^{O}/_{C}\right)_{pyro}\right)$
$\alpha' = \left(^{O}/_{C}\right)_{pyro} - \left(^{O}/_{C}\right)_{daf\ fuel} + \left(\frac{\left(^{H}/_{C}\right)_{daf\ fuel} - \left(^{H}/_{C}\right)_{pyro}}{2}\right)$
$\beta' = \left(^{H}/_{C}\right)_{daf\ fuel} - \left(^{H}/_{C}\right)_{pyro} + 2\left(\left(^{O}/_{C}\right)_{daf\ fuel} - \left(^{O}/_{C}\right)_{pyro}\right)$

3 Results and Discussion

A range of measurements has been conducted to analyze the performance of the new sampling system. Furthermore, as part of the project aims, measurements were conducted in cooperation with several other projects, using the new sampling system. Results that has been important to increase the understanding of the dynamics of different parts of the system and how to develop the methodology regarding the measurements has been summarized here in section 3.2. The projects and groups that has collaborated during this project, as well as related publications are listed in section 7. Note that the results included here are focused mainly on the development of the measurement methodology and further results can be found in the listed publications of the collaborating projects.

3.1 PERFORMANCE OF THE NEW SAMPLING SYSTEM

The system was used to measure the gas composition as well as the tar level and composition.

3.1.1 Gas Composition

A feasible agreement between the online PG-analyzer and the mobile μ-GC, while sampling the gas with the new sampling system upstream of the product gas cooler (point B). Figure 12 show an example of a period of parallel measurements of the concentrations of H_2, CO, CO_2 and CH_4 in the product gas and the comparison shows a reasonable agreement. Thus, there are no significant systematic errors in the measurements caused by the sampling systems, instrumentations or calibrations.

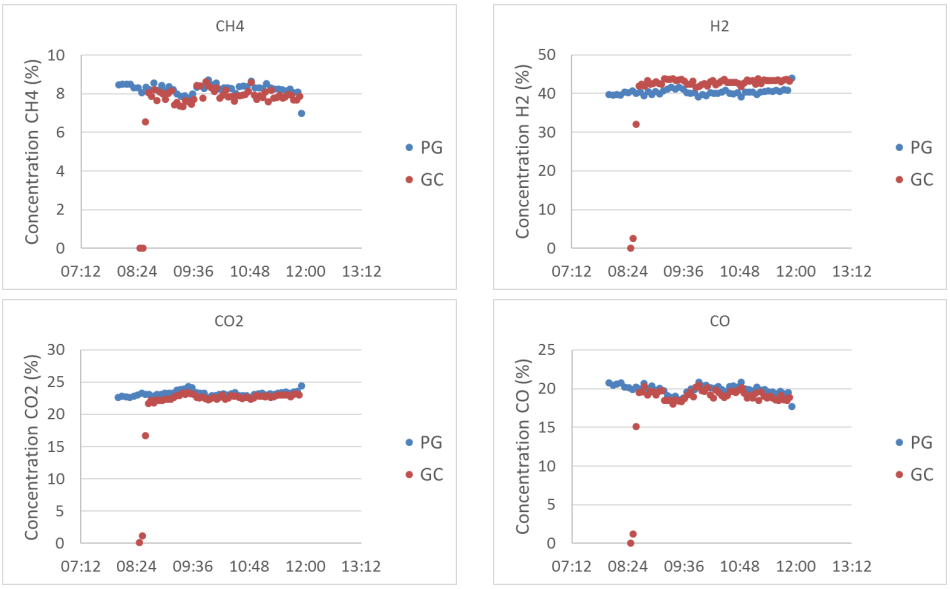


Figure 12: Comparing the concentrations of the major gas components measured with the GC and the product gas analyzed (PG) respectively.

Further investigation show that the composition of the gas sampled through the ceramic sampling-filter is in fact changing with time even though the temperature of the gas passing the filter was no more than 330 °C. Figure 13 show the gas composition measured with the μGC compared with the online analyzer during three different step: 1) after operating the sampling-filter without pulsing it for about 20 hours; 2) after pulsing the sampling-filter with nitrogen; 3) after switching to sampling the gas after the RME scrubber (point E). The time of the changes are indicated with dotted lines in Fig. 13.

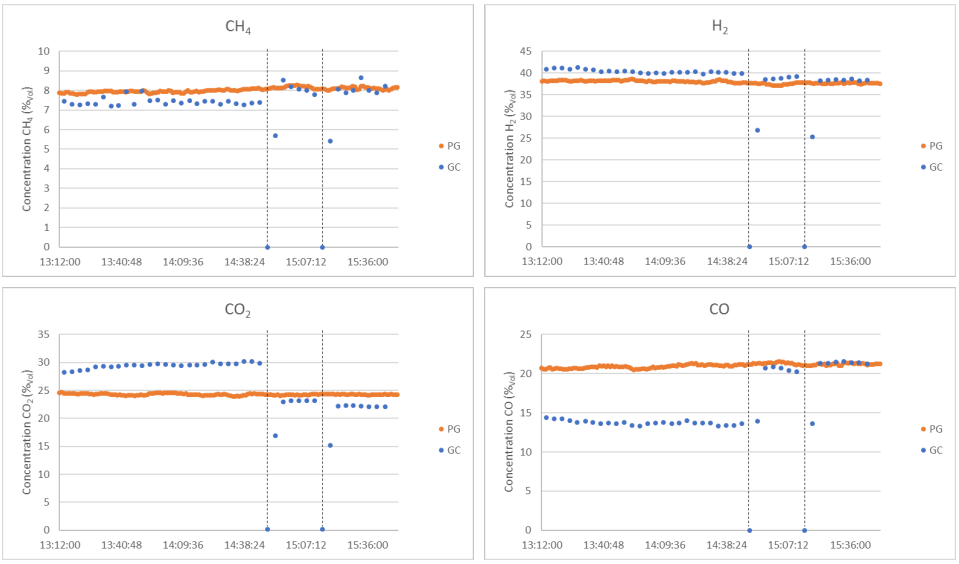


Figure 13: Comparing the measured gas concentrations with and without pulsing of the sampling filter as well as when sampling the gas from after the scrubber.

These measurements were made while nitrogen was used as purge gas in the process. Some purge gas is added in the product gas (PG) filter and the N_2 content is increased downstream of the PG-filter with about 1,6%vol as shown by Figure 14.

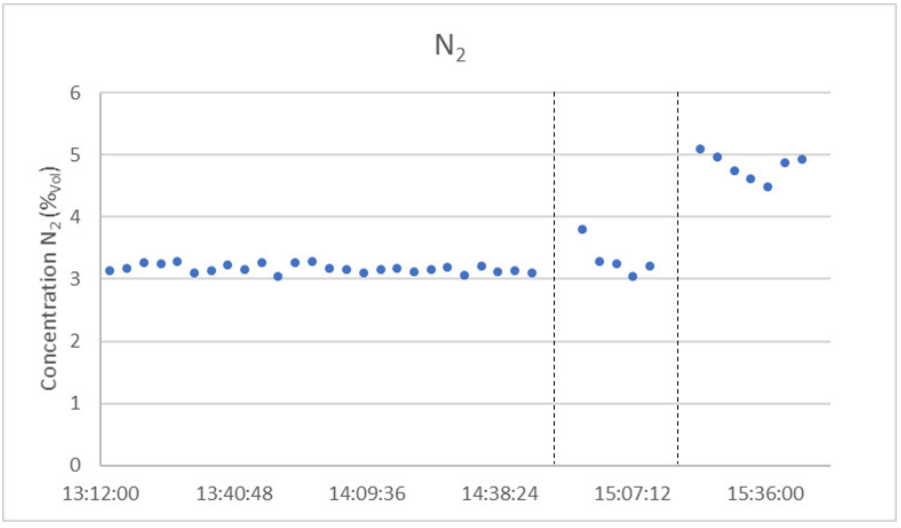


Figure 14: Concentration of N_2 measured with GC during the same time as illustrated in Fig. 13.

By studying the H/C and O/C ratios based on H_2, CO, CO_2 in a specialized Van Krevelen diagram, Fig. 15, it becomes clear that the water gas shift reaction cannot solely be used to explain the change in the gas composition and some additional reaction must have occurred. It is not clear at this time what reactions that can explain the change, but Fig. 15 show that either some organic compounds has been formed from the syngas or O_2, CO_2 has in some way been added to the gas. Further tests are required to understand the mechanism. However, the results show that to have a representative measurement of the product gas before the cooler, it is essential to pulls any filter in the sampling system to remove the filter cake. For a continuous online sampling and measurement of the product gas upstream of the product gas cooler, an automatic pulsing system would be required. Further, an extraction system of the particles would be required to empty the filter-house, or a redundant filter would be needed to remove the particles. Note that this became very clear even with a sampling probe, which was built with the gas inlets placed with 180 ° angel from the flow direction of the product gas and with a low velocity in the gas inlets. Hence, the effect is caused either by very fine particles that follows the flow path of the gas or by gas phase components that are condensed as the gas is cooled down in the probe, such as alkali salts.

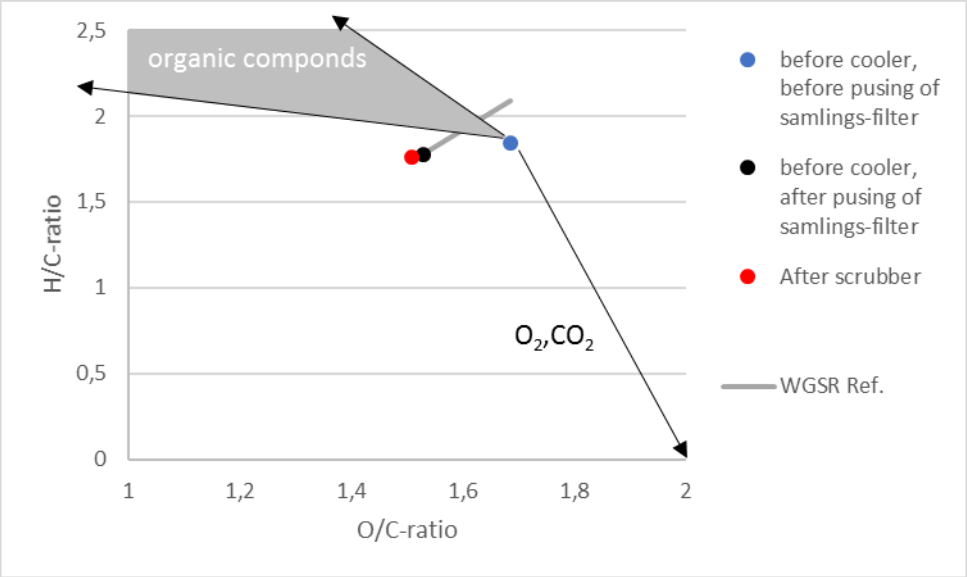


Figure 15: Van Krevelen diagram of the composition of the syngas (H_2, CO, CO_2) for measurements before and after pulsing the filter of the sampling system, and a reference measurement of the gas composition after the scrubber.

3.1.2 Tar Measurements

The concentration of tar in the product gas before entering the cooler was measured using the new sampling system, as well as with a specialized sampling probe as described in Section 2.2.2 and here referred to as "probe+amine". Adsorbents with an amine, is here referred to as "amine" samples, and the adsorbent including both an amine and activated carbon is here referred to as "carbon+amine". Measurements were conducted for 5 days to investigate if there are any difference in the results from the different methods. Figure 16 show the measured total amount of tar including BTX-components measured with the

different approaches, as well as the CH_4 concentration as a function of time. The results show that there are significant differences between the different approaches. Especially when sampling with only an amine straight from the 350 °C warm gas in the new sampling system the analysis shows a significantly lower result. As has been previously shown [10] there might be situations where the amine is not sufficient to capture light components, especially benzene, in a satisfying. Due to the high temperature, combined with the high steam content (in range of 30-40%), the temperature of the amine gets high during sampling, reducing the ability to adsorb some components.

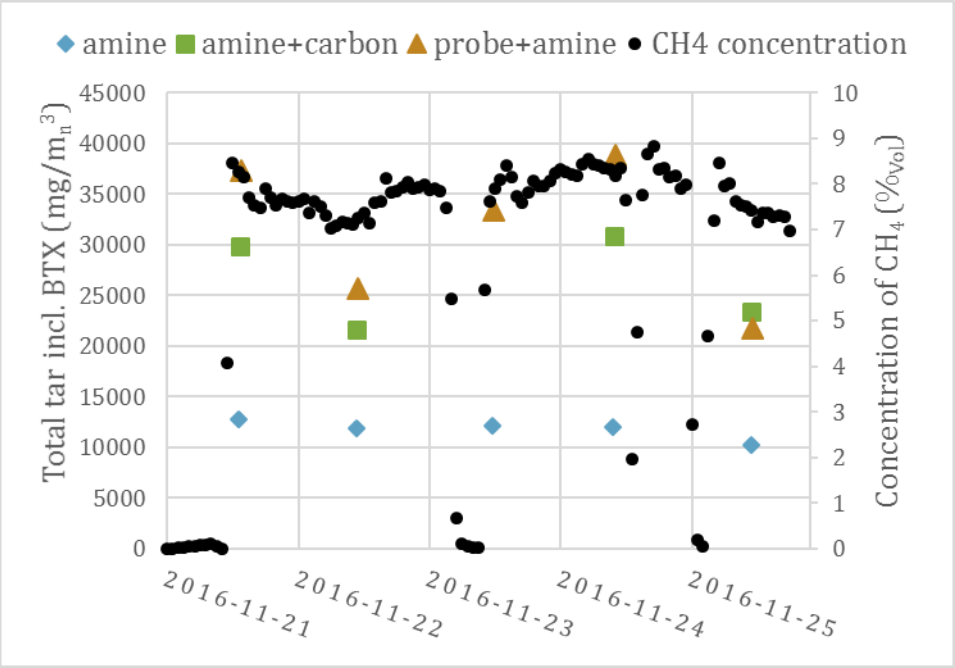


Figure 16: Comparison of results from three different approaches using the SPA method to analyze the amount of tar in the product gas during 5 consecutive days. The CH_4 concentration are included to indicate the activation of the bed material during the sampling period.

Figure 17 show the same comparison as Fig. 16 but, all components with less than 2 aromatic rings structures are excluded. Hence, components with a smaller molecular mass than Naphthalene are not included. Results show that even for these components there are a significant difference when using adsorbent with just an amine or the one with both an amine and activated carbon. Thus, it can be concluded that one should always use an adsorbent with both amine and activated carbon when sampling tar from a continuous gas flow with high steam content and temperatures of around 350 °C.

The tar level measured using the probe are for most cases higher than the tar level measured *via* the sampling system, especially for the cases when the activation of the bed material was low, as indicated by a higher CH_4 concentration. With a higher activation of the bed material in the gasifier, and thereby a lower CH_4 concentration, the tar level measured *via* the new sampling system are on a similar or even higher level than the tar level measured *via* the probe.

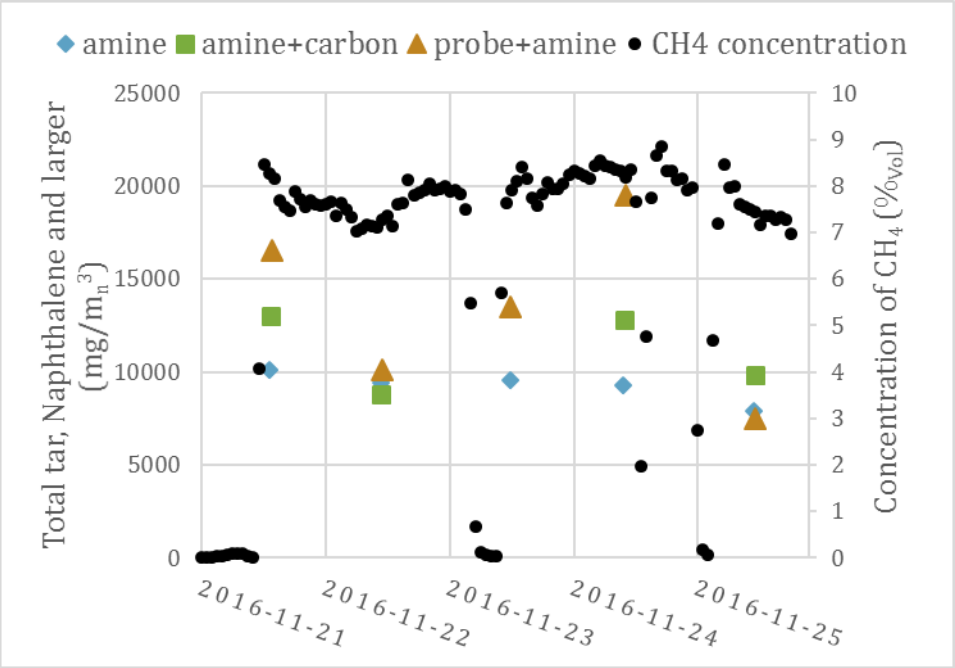


Figure 17: Comparison of results from three different approaches using the SPA method to analyze the amount of tar in the product gas during 5 consecutive days, excluding al known compounds lighter than Naphthalene from the analysis. The CH_4 concentration are included to indicate the activation of the bed material during the sampling period.

The difference in the results using the probe and the sampling system are further analyzed by comparing the composition of the tar as shown in Fig. 18. The tar components are divided into 6 groups with known compounds and one with all unknown compounds lumped, described in table 7. In Fig. 18 the filled bars represent the results for the "amin+carbon" samples and the unfilled bars represents the results of the "probe+amine" results. One can notice a significant difference in group 5 that includes the largest component, where a much higher fraction is measured when using the probe. Further, significantly less heterocyclic compounds, group 6, are measured using the probe, which indicates a more "mature" tar mixture when sampling with the probe compared to using the sampling system. In the sampling system the sampling gas is quickly cooled so that the "tar maturation reactions" are quenched in contrast to when sampling with the probe. When sampling with the probe, there is also a risk that additional tar components condense on the tip or even diffuse into the probe during the sampling which takes several minutes as several amines needs to be used. This could also cause an increase of especially large components with a high dew point.

The new sampling system includes a filter and it is of course a risk that the tar is affected by the filter, or rather by particles stuck on the filter. Previously it has been validated at Chalmers that this type of ceramic filter does not affect the tar measured with SPA [10]. However, the particles in the gas could differ for different gasifiers and different operational conditions and the buildup of a filter cake could affect the tar. To minimize this risk, the filter should therefore always be pulsed prior to sampling of tar.

When extracting tar containing gases there is always a risk of having some fouling in the sampling system due to cold spots. However, when estimating the dew point using the calculator at the thersites site [17], components with a dew point even below 100 °C differ significantly between the different sampling methods. The concentration of specific components and, thereby the estimated dew point changes up and down with time, even though the heating and setup of the sampling system remains constant. This, together with the very low dew point of the measured tar, makes it unlikely that condensation of tar components in the sampling system is the main cause for the difference between the methods.

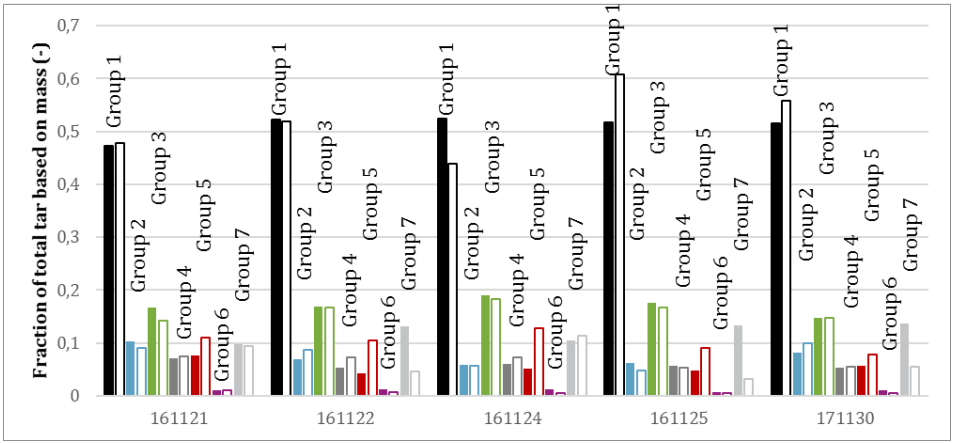


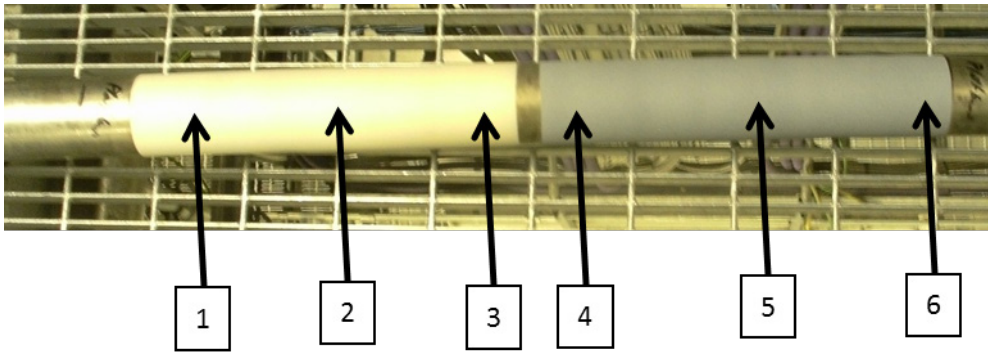
Figure 18: the fraction of the different tar groups for five different measurements based on the "amine+carbon" samples (filled bars) and "probe+amine" samples (unfilled bars). The groups are summarized and described in table 7 where the colors used for each group are also clarified.

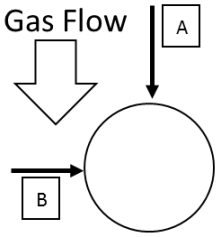
Table 7: Description of the different tar groups and the color used to visualize them in Fig. 18.

Group	Description	Color in Fig. 18
1	Benzene	Black
2	One ring components excluding Benzene	Blue
3	Naphthalene	Green
4	Two rings components excluding Naphthalene	Dark gray
5	Components with three rings and more	Red
6	Heterocyclic aromatic compounds	Purple
7	Unknown compounds	Light Gray

3.1.3 High Temperature Coating in Product Gas Environment

The status of the different coatings applied to the sampling probe was investigated after about 1.5 year in operation and the results are presented in Fig. 19. It was concluded that both coatings have suffered from attrition in the very harsh environment of the product gas line. Measurements of the diameter indicates that Coating 2 (ZrO_2) has suffered less attrition. However, it is unclear if there are significant differences in the flow pattern and particle load in the different parts of the product gas line and a more detailed study are required to draw more elaborated conclusions. Based on the level of attrition it was estimated that a new coating should be applied every 1-2 years, during the revision of the plant.





	Coating 2			Coating 1		
Measurement positions	**1**	**2**	**3**	**4**	**5**	**6**
A	60,27	60,39	60,34	60,20	60,26	60,45
B	60,31	60,27	60,38	60,28	60,21	60,09

Diameter before coating, 60,23 *Diameter before coating, 60,25*

Figure 19: Picture of the high temperature coating applied on the sampling probe and measured thickness at different locations after about 1.5 year of operation.

3.2 CONTROL PARAMETERS

The operation of the GoBiGas-gasifier has been significantly simplified by identifying useful control parameters that delivers online information on the performance of the gasifier. The first one is the CH_4 concentration that is used as a control parameter for the level of tar in the gas. This is based on the correlation between the CH_4 concentration and the tar concentration in the product gas as described below. Second one is based on the concentrations of H_2, CO, and CO_2 in the product gas that is used to estimate a Syngas modulus, hence a measure on how well the fuel in the gasifier is transformed into a pure syngas.

3.2.1 Methane and Tar Correlation

The correlation between tar and CH_4 in the GoBiGas gasifier has previously been published [15] and as shown in Figure 20 the results from that study reveals that there is a strong correlation with both the total tar yield and specific tar components, such as Chrysene.

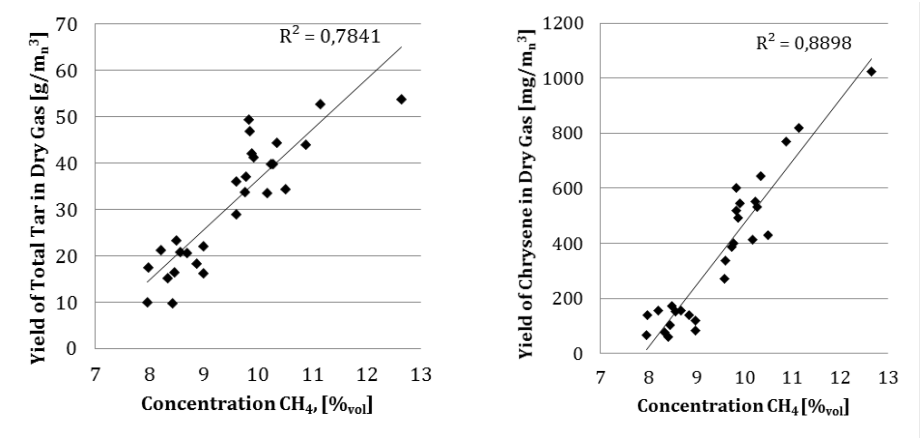


Figure 20: Correlations between the CH_4 concentration and total tar incl. BTX (left) and the largest identified tar component Chrysene (right) when operating with wood pellets.

The correlation between tar and the CH_4 Concentration was further investigated using the CON-TAR that is a prototype built by TU Berlin to yield an online, qualitative measurement of the tar concentration. Figure 21 shows the results from a 66 hour continues measurement from startup, with initially very low concentrations, to stable operation. The results indicate that a linear correlation is only feasible for a specific range and when including lower CH_4 concentrations a logarithmic correlation fits the data better. However, for typical range of CH_4 concentrations (8.3-8.8%$_{vol}$ with wood pellets) a linear correlation has been found to work just fine.

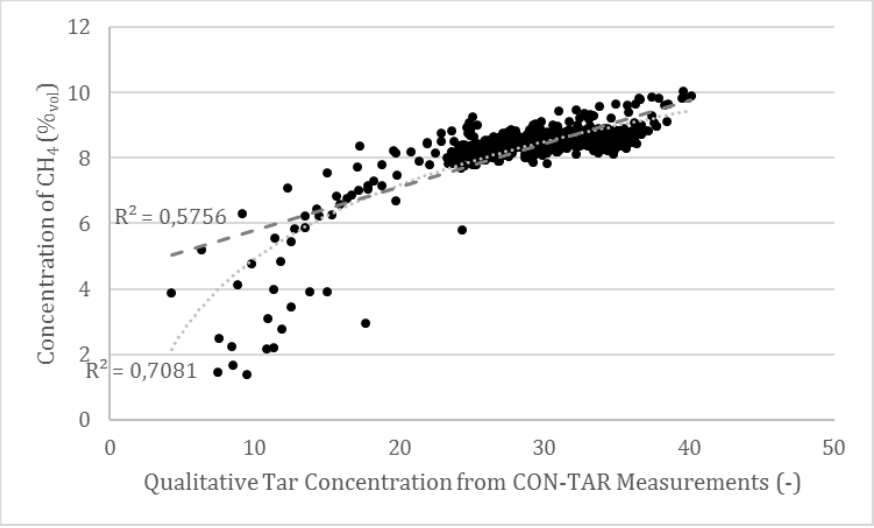


Figure 21: Correlations between the CH_4 concentration and qualitative amount of tar measured with CON-TAR.

Different fuels have been gasified in the GoBiGas-Gasifier and Fig. 25 show the tar and CH_4 correlation using different fuels. Results shows that it is required to establish a specific correlation for each fuel. Several parameters, such as fuel moisture, gasification temperature, fuel load, ash content and composition, change

when switching fuel type and further studies are required to describe why this difference occur.

The method of using the CH_4 concentration as a control parameter has successfully been implemented at GoBiGas and has been crucial to avoid clogging of the product gas cooler, especially due to tar deposits. By increasing the fed of potassium to the process when the CH_4 concentration gets too high, and *vice versa*, the tar level can be limited. However, if too much potassium is added to the process there is a risk that the product gas cooler gets clogged by potassium rich deposits and a lower limit for the methane should also be established. This is arbitrary visualized in Fig. 25 with red dotted lines. When the goal of the process is to produce CH_4, which is the case with the GoBiGas-plant, there is also no point of reducing the CH_4 concentration more than necessary to avoid tar problems. Typical ranges for the CH_4 concentration given to the operators for different fuels are summarized in Table 8.

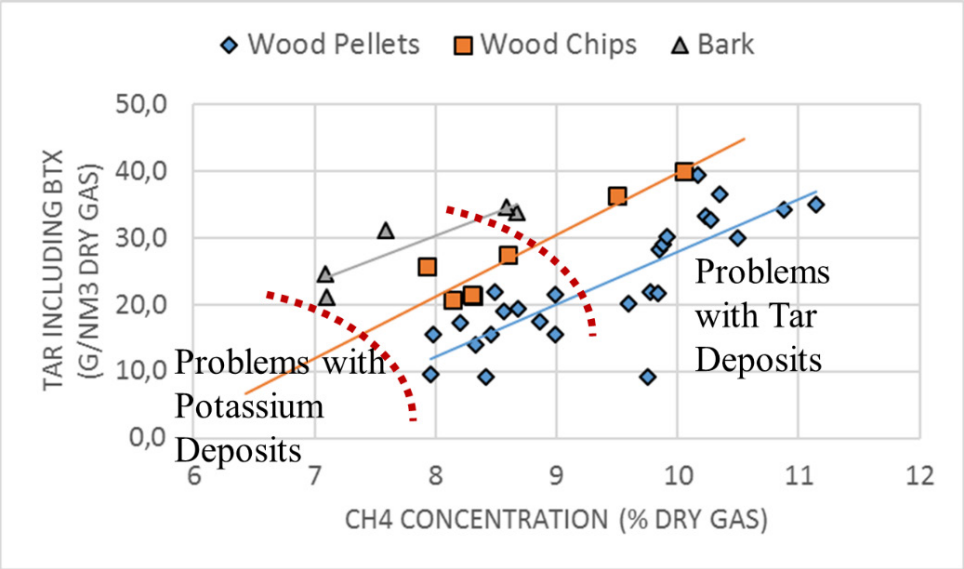


Figure 25: total tar yield including BTX as a function of the CH_4 concentration for different fuels and a rough indication on the, for GoBiGas, appropriate operational area.

Table 8: Summary of the recommended CH_4 concentrations for different fuels

Fuel type	Recommended CH_4 Concentration
Wood Pellets	8.3-8.8 $\%_{vol}$
Wood Chips	8.1-8.7 $\%_{vol}$
Shredded Bark	8.0-8.6 $\%_{vol}$

3.2.2 Syngas Modulus

The syngas modulus, defined in section 2.3, is a measure on how well the biomass is converted into pure syngas, here referring to H_2, CO and CO_2. A syngas modulus of zero corresponds to the gas released during pyrolysis and a syngas modulus equal to 1 corresponds to a complete conversion of the fuel into pure

syngas. A higher syngas modulus indicates a higher conversion of char and hydrocarbons like CH_4 or tar, but the modulus is also affected by the addition of oxygen or CO_2 to the gas. Adding a lot of oxygen could in fact generate a negative syngas modulus. The syngas modulus is proportional to the chemical efficiency of the gasification and it can, thereby be used as an indicator of the impact oxygen addition has on the chemical efficiency. An example is the use of an active bed material that transport a significant amount of oxygen such as Ilmenite or Bauxite [16] where the syngas modulus can be used to indicate if the increased conversion of hydrocarbons and char can compensate for the efficiency loss as part of the syngas is oxidized by the bed material.

Figure 26 show the correlation between the total tar yield as a function of the syngas modulus for the GoBiGas-Gasifier when operated with wood pellets as fuel and olivine as bed material. Figure 26 show that the correlation between these parameters is lower than between the CH_4 concentration and tar concentration (Fig. 20). Thus, the CH_4 concentration is better suited as an indicator for the level of tar in the product gas. Instead, the syngas modulus is better used as an indicator of the overall fuel conversion as the syngas modulus is also affected by several other parameters.

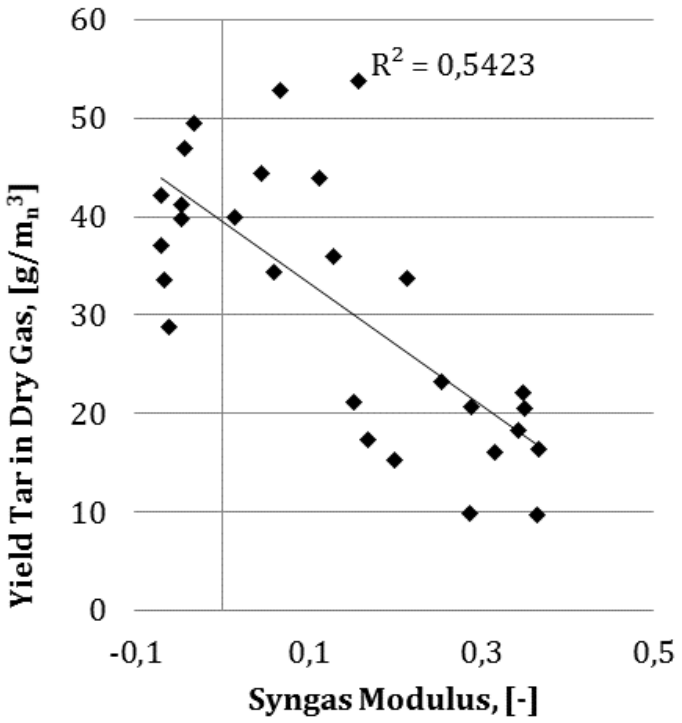


Figure 26: Yield of total tar including BTX from the GoBiGas-Gasifier operated with wood pellets as a function of the Syngas modulus. From Larsson *et al. [10]*

Figure 27 shows the syngas modulus, CH_4 concentration and feed of potassium as a function of time during three consecutive startups of the GoBiGas-Gasifier. During heating of the process, the activation of the bed material is lost to some extent when the process is heated with an ash free fuel, in this case, natural gas [15]. Therefore, it is very important to monitor the activation during startup to

know how much potassium that should be added to the process. Figure 27 illustrates low values of the syngas modulus and high CH_4 concentration initially during startup and how this is counteracted by feeding a lot of potassium to increase the activation of the bed material.

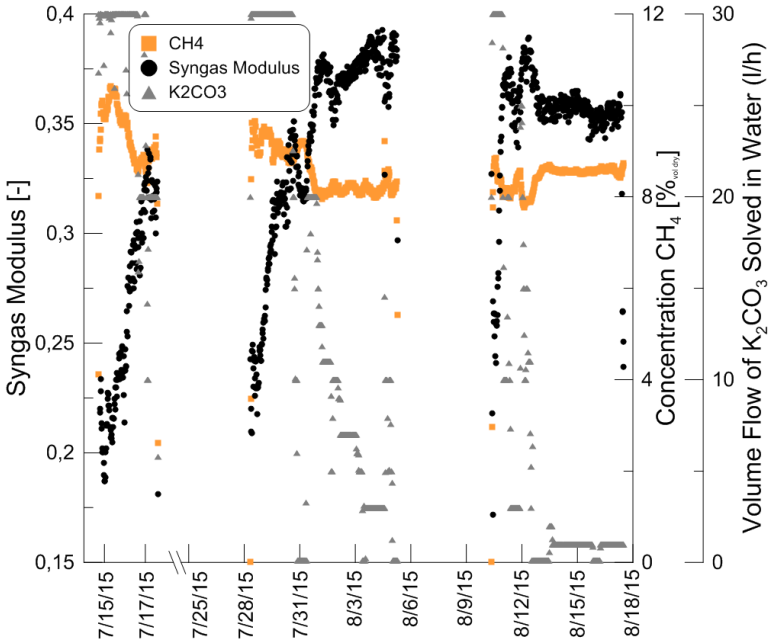


Figure 27: Syngas modulus, CH_4 concentration and feed of potassium during three consecutive startups of the GoBiGas-Gasifier. From [7]

3.2.3 Online Tar Measurements at Different Positions of the Process

The new sampling system has enabled parallel connection of different measurement equipment, and to shift between the measurements points upstream of the PG-cooler, downstream the PG-filter, and downstream of the scrubber (points B, C and D in Fig. 3). This was utilized to investigate the dynamics of the cleaning section of the GoBiGas process by measuring the tar level online with CON-TAR in parallel with measurements of the permanent gases using a µGC while also sampling with SPA from the same gas. Figure 28 show the qualitative level of tar measured with CON-TAR and the nitrogen content measured with the µGC.

The N_2 concentration is here used as a quality check for the sampling show that there is no major sampling issue during the measurements. The concentration of N_2 is slightly higher downstream of the product gas filter and downstream the scrubber as the filter are pulsed with nitrogen. Note, that the measurements were conducted when the gasifier was operated at an unusually low load due to issues with the fuel feeding, and that the nitrogen is later replaced with CO_2 as purge gas when produced further downstream, lowering the N_2 concentration well below 1% in the produced biogas.

The measurements with CON-TAR yields a qualitative value of the total amount of tar in the wet gas mainly including Naphthalene and larger components (see section 2.2.2 and [13] for further details). The difference in the qualitative tar level

before the cooler and after the filter show that a significant amount of tar is removed by the filter. The SPA analysis shows a reduction of about 15-25% of Naphthalene and larger components, where it is mainly the largest tar components that are removed. However, the online measurements reveal that the tar level after the filter fluctuates significantly as the filter is pulsed. It might therefore be challenging to quantifying the true effect of the filter using an offline method such as the SPA method. This also shows that it is not appropriate to sample gas downstream of this type of product gas filters if one is to measure tar or test equipment with a slipstream of gas.

The tar level is further reduced after the scrubber where the majority of large tar components are removed, and only small fraction of Naphthalene remains. SPA show that about 0.5g/m_n^3 of Naphthalene is not captured by the RME during the investigated operational case. The CON-TAR measurements show that in spite the fluctuation in the tar content before the scrubber the level after the scrubber is stable.

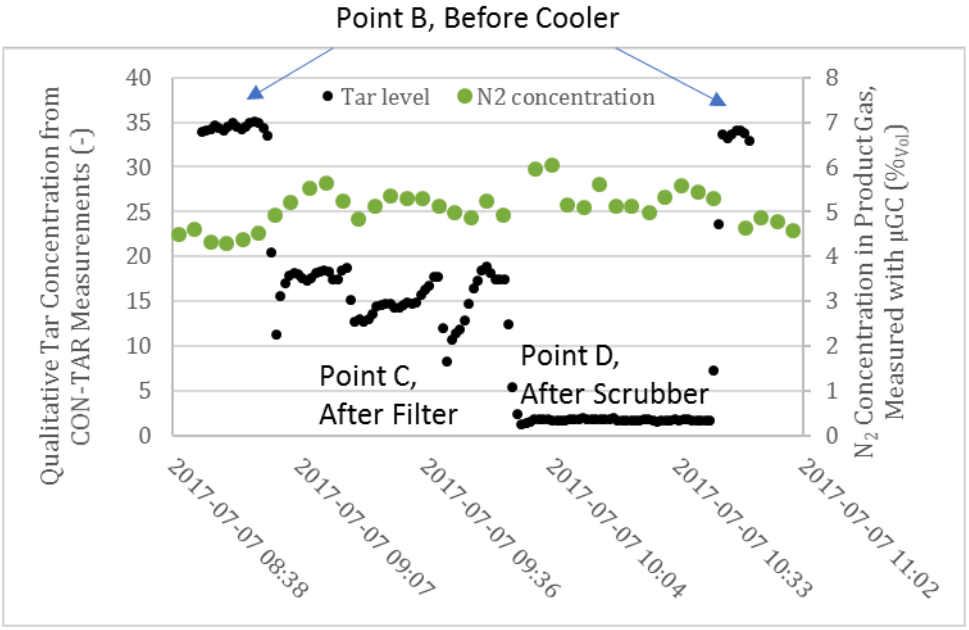


Figure 28: Qualitative measurement of the total level of tar (Naphthalene and larger) and the nitrogen content while measuring at different points of the process.

Measuring with CON-TAR at different points of the process has revealed a potential of utilizing a simplified setup of the LED-based CON-TAR system to monitoring the performance of the primary cleaning step, which at GoBiGas consist of a RME-scrubber. Therefor a new, simplified, prototype of CON-TAR has been developed together with the BioProGReSs project and TU Berlin and has been installed for testing at GoBiGas. The goal is to simplify the optimization and monitoring of the RME-scrubber. This is something that is very important for the development of the process as the RME- constitutes a rather large portion (5-10%) of the operational cost and should be minimized while at the same time an increased slip of Naphthalene would increase the strain of the adsorbent beds downstream of the scrubber.

3.2.4 Online Benzene Measurements Downstream of the Adsorbent Beds of Activated Carbon

There are 1 pre-adsorber and 3 bulk-adsorbent (step 8 Fig. 1) used to remove the remaining tar downstream of the RME-scrubber. Tar components larger than Naphthalene should be adsorbed in the pre-adsorber which is operated in series with bulk-beds. The bulk-beds are operated batch-wise to adsorb aromatic compounds such as Naphthalene, Toluene, Xylene and Benzene, then being regenerated with steam and the cooled. The Benzene has the highest concentration in the gas prior to the adsorbent beds and are the limiting component determining the operational hours of a carbon bed before it needs to be regenerated. It is also the lightest of the aromatic compounds consisting of only one ring-structure and no branches and can be expected to be the first aromatic component to slip from the bed when it has reach its full adsorption level.

To avoid extensive carbon formation on downstream catalysts the concentration of aromatic compounds must be limited. Therefore, the mobile µGC was used to measure the concentrations in the gas downstream of the carbon beds to monitor the performance of the carbon beds and to better understand how the operation of the carbon beds affects down-stream process steps. Figure 29 show the concentrations of C_2H_2, C_2H_4, C_2H_6 and C_6H_6 (Benzene) as a function of time over several adsorption cycles. The end of each adsorption cycle is indicated with a dotted line and it can be seen how Benzene starts leaking in the end of some of the cycles.

During cooling of a regenerated bed, the regenerated bed is phased-in in series upstream of the carbon bed currently in use. As the newly regenerated carbon bed is put in operation (initially cooled with product gas), the concentrations of olefins and especially C_2H_4, drops with up to about 25% of its initial concentration. This will affect the downstream reactor used for hydrogenation of olefins and the measurements shows that a smother shift is important to avoid variations in the gas concentrations after the adsorption beds.

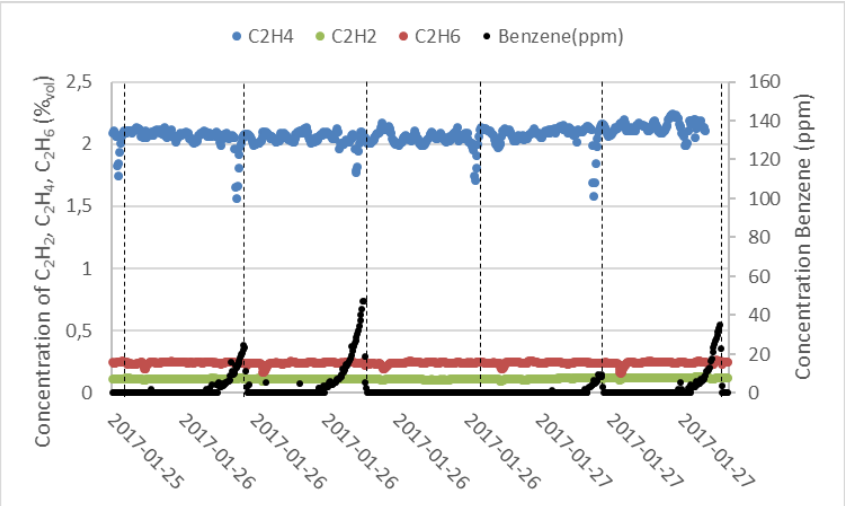


Figure 29: Concentrations of Benzene and olefins (C_2H_2, C_2H_4 and C_2H_6) after the adsorption beds of activated carbon

The online measurements of Benzene proved very useful for the monitoring and optimization of the adsorption beds and an online industrial GC has been installed to measure the Benzene concentration. Figure 30 shows an example from the initial test with the new online Benzene detector for a number of adsorption cycles. During the tests it was detected that one of the beds underperformed causing a higher Benzene concentration than can be tolerated, but with this knowledge the operation of the beds could be adapted to avoid high benzene slip. With the Benzene analyzer the operation can now be adapted to fit the performance and status of each individual carbon bed and thereby optimize the performance.

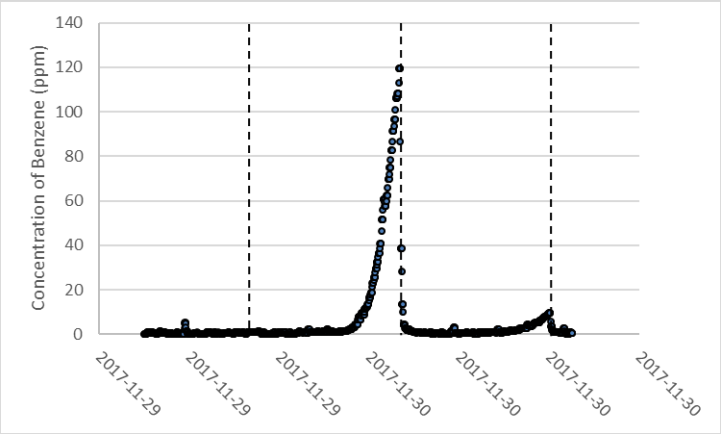


Figure 30: Concentration of Benzene after the adsorption beds of activated carbon measured with the new online GC-FID installed at GoBiGas

3.2.5 Online Measurement of Alkali Components in the Product Gas

As alkali in the form of potassium is crucial for the gasification process at GoBiGas to limit the level of tar in the product gas but also can cause clogging of the product gas cooler, measurements were conducted to monitor the alkali and particle content of the product gas. Measurements were conducted during startup as well as during continues operation and the results has been published by D. Gall *et al.* [8]. Some of the results are included here as they gave important understanding of the process and how to improve the methodology regarding measurements at a process like GoBiGas. Figure 31 show that the alkali concentration in the product gas during start up, before adding any fuel to the gasifier, are very low even as potassium is added to the process. This show that the risk of clogging the cooler during the heating of the process is low but it also shows that it can be difficult to detect if the bed material has been properly activated with potassium prior to start of the gasification by measuring the alkali concentration.

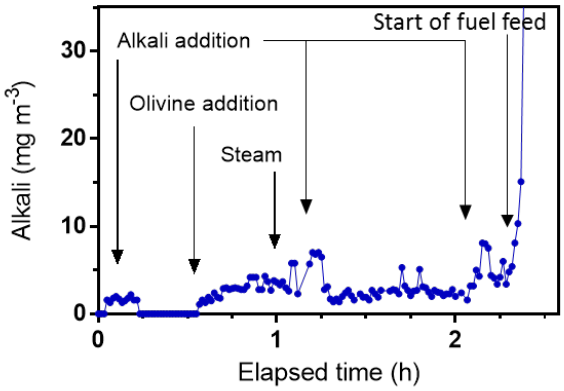


Figure 31. Potassium concentration during about 2 hours prior to the start of fuel feeding. Adapted from D. Gall *et al.* [8]

As fuel is feed to the gasifier the concentration increases rapidly as shown at the end of Fig. 31 as well as in the beginning of Fig. 32 that show the alkali concentration as well as the particle concentration in the product gas. During continuous operation the alkali concentration and the particle concentration increase drastically as the fuel feed is started. As more potassium are added to the process to increase the activation of the bed material the concentration in the gas increase. At the end of the operational period depicted in Fig. 32, too much potassium was added to the process and the concentration of alkali increased significantly before the pressure drop over the cooler started to increase exponentially due to deposits in the entrance of the cooler (further described below, see Fig. 34) forcing a stop of the process. The concentration of alkali in the gas, that a process can cope with without sever amount of deposits depends on the design of the cooler and the temperature of the gas at the inlet and a concentration limit that is general for all processes is unlikely. However, the results show that an online measurement with a SID can be a useful tool for avoiding too high concentrations of alkali in the product gas.

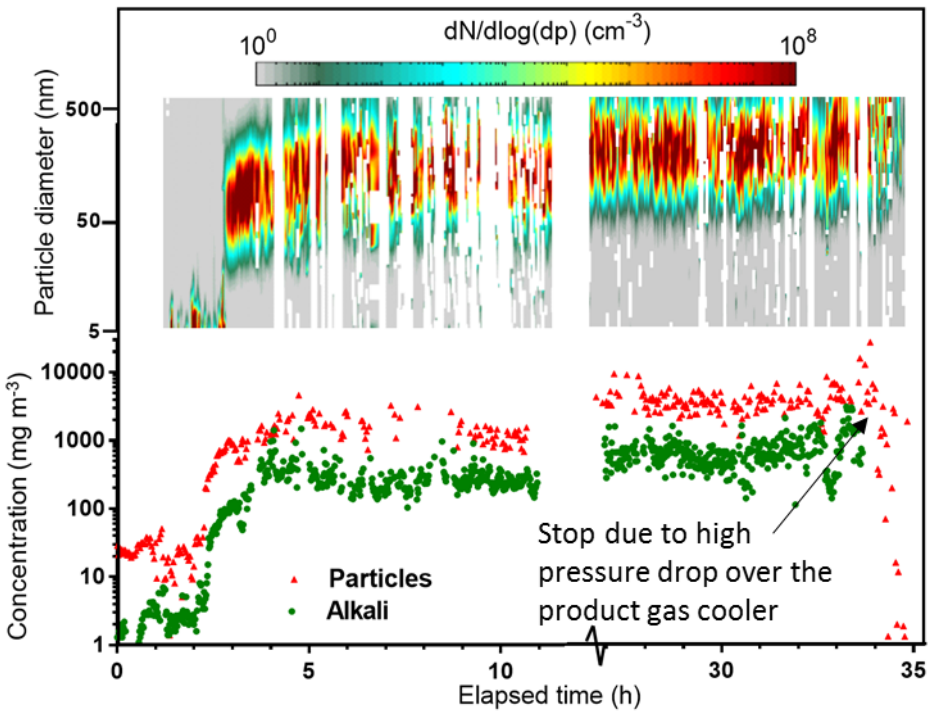


Figure 32: Concentration of potassium (lower) and particles (upper) in the product gas. Adapted from Gall *et al.* [8]

The same sampling system as used for the measurements with the SID can be used to monitor the concentration of particles in the product gas. Figure 33 show the particle size and concentration in the product gas at different states of operation. During warmup of the process, purge gas (N_2) is used to fluidize the gasifier and before starting the fuel feed the fluidization is switched to steam. During these steps, only very small particles becomes entrained and passes through the product gas cooler to the filter. When the fuel feeding is initiated, larger particles gets entrained, and as the fuel load increase larger and larger particles are entrained in the product gas.

Experience from the GoBiGas plant shows that with a low gas velocity in the gasifier and through the product gas cooler, there is a tendency to clog the cooler with fines. This leads to an increase in both the pressure drop over the cooler and an increased gas temperature after the cooler. However, in contrast to the deposits of tar or ash this can be reversed by increasing the gas velocity or introducing fine bed material particles. This will cause entrained particles to leave the gasifier with the product gas and pass through the cooler, removing the deposits of very fine particles. Thus, it can be useful to map the size and concentration of particles leaving the gasifier, especially to enable operate the gasifier at a partial load.

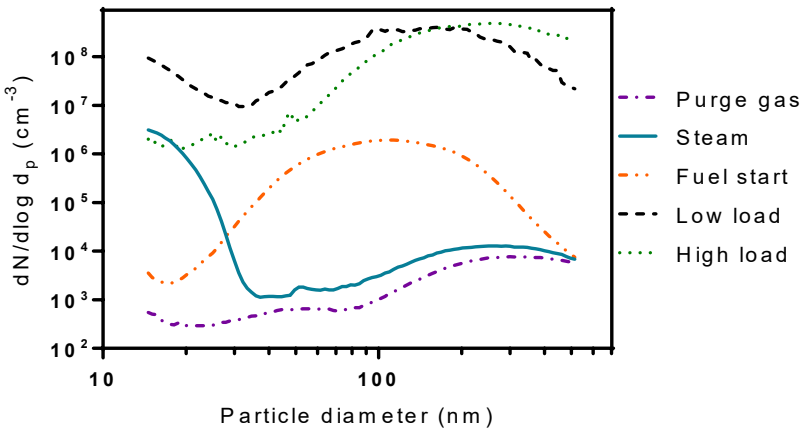


Figure 33: particle concentration in the product gas during different stages of the process start up until continuous operation with high load. Adapted from Gall *et al.* [8]

The ash deposits formed in the entrance of the product gas cooler is shown in Figure 34 and the analysis of the composition confirms that there is a high concentration of ash components and especially potassium, as shown by the results of the XRF analysis. Note that the picture only shows the deposits from the very top of the cooler, where one can clearly see the entrance to the tubes of the cooler, but deposits are also formed in the tube entrance, which could not be captured on photo in a satisfying way. The XRF analysis is not comprehensive, and for instance, magnesium that is the major component of the olivine bed material are not included, but the presence of Fe and heavy metals indicate that some bed material is stuck in the deposition, but the major components are potassium and calcium. As part of the deposits are solvable in water, and even more so in acid, a significant part can be assumed to be salts.

As the product gas is cooled, it will become saturated alkali salts that will condense or form particles depending on the temperature. Thus, by carefully monitoring and controlling the temperature before the cooler one could make sure that the alkali components are in solid phase before entering the cooler to avoid clogging. This could be an alternative approach to controlling the concentration of alkali in the gas phase, or, the methods could even be combined to monitor both the concentration of alkali and temperature of the gas before the cooler, yielding an efficient tool to monitor and reduce the risk of alkali components condensing and clogging the cooler.

Element	PPM	+/-
K	156202	3287
Ca	136821	2812
Ti	428	64
Cr	1338	41
Mn	1920	52
Fe	6613	70
Ni	141	9
Cu	31	4
Zn	72	3
As	3,3	0,8
Rb	16	1
Sr	28,5	0,9
Zr	7,8	0,8

Figure 34: Picture of ash deposits extracted from the top of the product gas cooler and the results of the XRF analysis of the deposits.

3.3 MEASURMENTS FOR EVALUATION OF THE GASIFICATION PROCESS

One purpose of current project was to enable the measurements required to establish a mass balance of the gasification part of the process and to quantify undesired components, such as tar, and identify where these ends up in the process. By utilizing the new sampling system developed in this project, comprehensive measurements of the product gas composition could be conducted, quantifying the gas components using a μGC and tar components using the SPA method. Thereby, the mass- and energy balance of the gasifier can be evaluated and used to evaluate important process parameters.

3.3.1 Carbon Conversion in the Gasifier and Undesired Components in the Gas

The carbon conversion in the gasifier was evaluated in cooperation with the project "char conversion in fluidized bed indirect gasification" where one aim was to quantify the char conversion in the GoBiGas-gasifier. The char conversion for two different fuels and different moisture content are showed in Fig. 35 together with the chemical efficiency to illustrate how the char conversion affects the efficiency of the process. The raw gas efficiency, denoted *eff RG*, are directly proportional to the char conversion as the raw gas include all of the gas produced in the gasifier including tar. The cold gas efficiency, *eff CG,* and biomass to biogas efficiency, *eff CH4*, are instead more dependent on the other process parameters as described in section 3.3.2 but are also limited by the raw gas efficiency. The results show that a higher moisture content tends to come with a lower char conversion and, thereby a lower raw gas efficiency. Further analysis, including how different operational parameters affects the char conversion and features affiliated with scale up of the process, and how this could affect the char conversion as well as the raw gas efficiency can be found in the following reference [18].

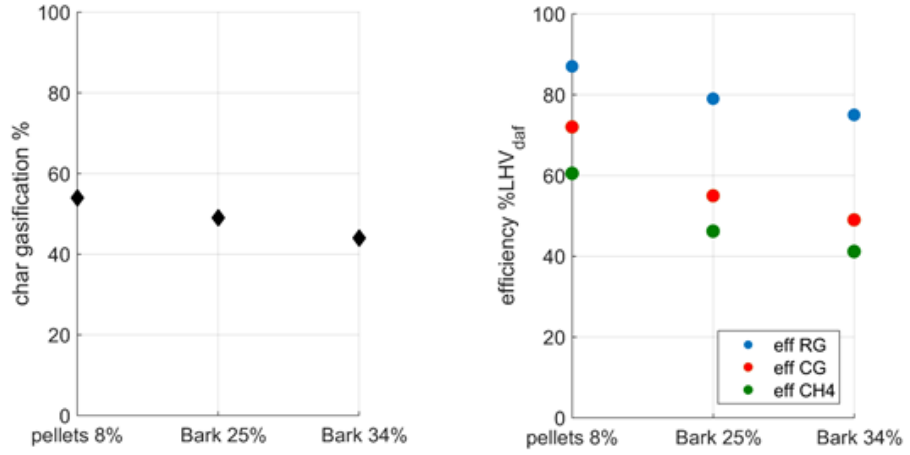


Figure 35: the estimated char conversion (left) and efficiencies (right) for three different operational cases. Adapted from Pallares *et al.* [18].

3.3.2 Mass- and Energy-Balance of the Gasifier for Performance Evaluation

The measurements of the gas and tar components in the product gas during operation with wood pellets has been evaluated in cooperation with the Chalmers node of the Swedish Gasification Center (SFC). Based on these results the performance of the process and possible improvements was assessed and published [2]. Figure 36 shows the performance of the GoBiGas plant and how changes in some of the major operational parameters would affect the chemical efficiency of the process where η_{RG} represents the raw gas efficiency (including tar and recirculated gas), η_{CG} represents the cold gas efficiency, and η_{sect} represents the biomass to biomethane efficiency. Results show that it is technically feasible to a achieve a biomass to biomethane efficiency of over 80% [2].

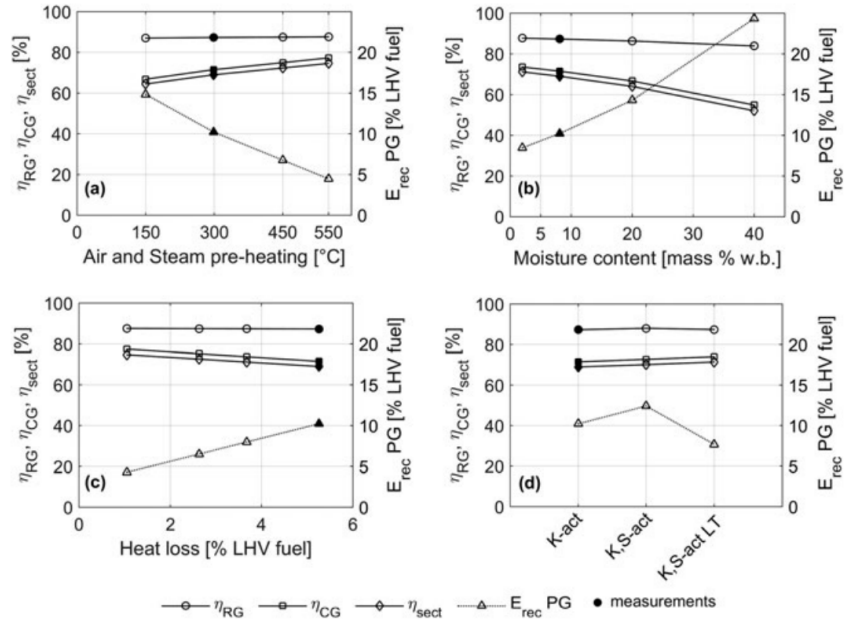


Figure 36: Chemical efficiency as function of a) air and steam temperature; b) fuel moisture content; c) heat loss; and d) different cases of additive addition. The solid dote corresponds indicates measured values while the other dotes are extrapolations.

3.4 ASSESMENT OF THE FULFILMENT OF THE PROJECT AIMS

The purpose of this project was to establish a new sampling system to enable measurements and testing with new equipment at GoBiGas. The goal is to improve the evaluation of the GoBiGas process, facilitating the testing of new equipment, and to develop the methodology for measurements at industrial scale DFB gasifiers. A number of measurable aims were established in relation to the project purpose and these are assessed below.

Aim 1: To increase the scientific level of the evaluation of the GoBiGas-plant, a method should be established to quantify the carbon conversion in the gasifier as well as the yield of undesired organic compounds, such as tar.

Assessment of Aim 1: The carbon conversion as well the yield of undesired components has been quantified a published in a scientific paper. The quantified carbon conversion has also been further evaluated and analyzed in a cooperating project report "Char Conversion in Fluidized Bed Indirect Gasification". Aim 1 is thereby considered fulfilled.

Aim 2: To establish a sampling system that enables the sampling of the gas produced in the gasifier for analysis in at least 2 parallel measurement systems, yielding complementing information.

Assessment of Aim2: Parallel measurements has been conducted for more than 6 hours using CON-TAR and a μGC system which was even further complemented by measuring the tar level using the SPA method. Satisfying performance of the sampling system and high-quality results was achieved and the aim was fulfilled.

Aim 3: Investigate the performance of the new sampling system regarding tar and gas measurements.

Assessment of Aim 3: The tar and gas sampled through the new sampling system has been compared with alternative methods in this report and the dynamics of sampling system has been investigated. It has been concluded that it is imperative to have a clean particle filter to yield representative results. The aim is regarded as fulfilled and important insight regarding the challenges of sampling this type of gas has been reached.

Aim 4: Arrange measurements with collaborating projects using the new sampling system to demonstrate new measurement techniques or gas conditioning equipment. In line with this aim at least 2 relevant measurement campaigns should be performed in cooperation with other projects.

Assessment of Aim 4: A long range of measurement campaigns has been performed in cooperation with several different projects and these are listed in Section 7 together with related publications that includes data or insights gain as part of current project. This aim has been fulfilled.

4 Methodology for Measurements at a Commercial-Scale DFB-Gasifier

An improved methodology for measurements has been developed for the GoBiGas-plant. In the following section the development is summarized, and it is discussed in more general terms, what and how to measure at a commercial scale DFB-Gasifier. The discussion is mainly focused on how to monitor and control the gasification process but also includes some additional measurements that are required to evaluate the process in detail.

4.1 MONITORING AND CONTROL OF THE PROCESS

It is crucial to be able to monitor and control the gas quality from the gasifier to avoid operational problems downstream of the gasifier. The experience from the GoBiGas regarding monitoring and control of the process is here discussed concerning start-up and continuous operation separately.

4.1.1 Continuous Operation

A commercial scale DFB-Gasifier can be expected to be equipped with the possibility to measure the main gas components of the product gas online, downstream of the primary gas cleaning steps. The gas should be clean enough to be conditioned and analyzed with standard equipment, such as the NDIR used at GoBiGas to measure CH_4, CO and CO_2. This is also complemented by measuring H_2 using a TCD and, for safety, O_2 using paramagnetic measurement. As established during this project these standard measurements can be utilized to monitor much more than just the concentration of the specific compounds, thereby possibly avoiding the need for more complex and expensive equipment.

If the DFB-Gasifier is operated with a bed material that enables significant amount of alkali salts to be available in the process, such as olivine, potassium can be used to control the gas quality and limit the yield of tar. As shown here it should not be necessary to have any complex sampling and measurement system to directly measure the level of tar. Instead a good correlation between the concentration of CH_4 and the total yield of tar has been identified and are being utilized to control the gas quality. This correlation can be expected to be plant specific and fuel specific during, and the commissioning of a new plant, suitable boundaries for the methane concentration should be established. The most crucial is to identify at which point one can avoid significant fouling in the downstream cooling surfaces. This limit will depend on both the gasification process, as well as the design of the cooling section of the process.

The GoBiGas-Gasifier has been operated in a wide span of operational cases and different fuels including wood pellets, wood chips and shredded bark. In general, a methane concentration below 8.5% has been shown to be sufficient to maintain a product gas temperature of about 200 °C after the product gas cooler without further clogging of the cooler. The appropriate CH_4 limits can be established through trial and error; however, this might be both costly and time consuming.

Therefore, it might be worth to measure the actual tar levels at least during the commissioning to establish a correlation between methane concentration and level of tar in the product gas. A multitude of methods and approaches for measuring tar exists and it is outside of the scope of this project to assess them all, but a few of them has been tested during the project and some features of these methods are summarized here.

The SPA method is a well-established method to sample and analyze the tar offline. The sampling can be rather quick and easy, but it is very important to sample in a correct way to quantify all the tar components as described in section 3.1.2. The method enables accurate quantification of specific tar components and provides detailed information about the composition of the tar. However, the analysis and preparation of samples is time consuming and requires access to lab environment. In general, results can at the quickest be available the day after and the samples only represents a brief moment of operation and the process dynamics are easily missed. The SPA method is well suited for establishing a correlation between the methane concentration and the tar level and can be useful for optimizing the gas cleanings steps of the process during commissioning to later be phased out.

Another approach for quantifying the total amount of tar is to extract a small slipstream of gas for continuous analysis. By reforming the gas using a high temperature reactor (HTR) developed by Chalmers University of Technology and that is operating at 1700 °C, the product gas can be reformed into a pure syngas that can easily be analyzed with standard equipment. This enables an indirect measure of the amount of tar as well as the total carbon conversion in the gasifier. By comparing the concentrations of the syngas components (H_2, CO, CO_2) in the reformed gas with the concentrations in the product gas a lot of information about the fuel conversion can be retrieved without complex measurement equipment. However, continuous operation at 1700 °C is challenging and redundancy is recommended if the approach is to be used for continuous monitoring the process. It can, however be an appropriate method to be used during the commissioning to establish the tar and CH_4 correlation.

The dynamics of the gasification in the form of fluctuations in the level of tar can be studied using LED based online tar measurement such as the tested prototype called CON-TAR, developed by TU Berlin. The technology is still at the prototype level but, has proven a useful complement to the SPA method by allowing qualitative online measurements and monitoring of the tar level in the product gas. A promising option is to use a simplified version of CON-TAR to monitor the tar level after the primary gas cleaning step which could enable optimization and even control of the performance of this important part of the process.

If the process is to be used to synthesize e.g. biofuels, such as the biogas produced at GoBiGas, a secondary tar cleaning step might be required to remove light aromatic compounds such as Benzene. The installation of an online GC to measure the concentration of Benzene after this step has been a crucial improvement at GoBiGas enable minimization of Benzene slip and increased utilization of the adsorption beds and an online Benzene analyzer should be considered for a commercial plant of this type.

Regardless of the approach used to measure tar it is important to focus on the sampling of the gas to get representative results. In general, it becomes more complex to sample the gas, the closer to the gasifier one gets, while at the same time more information about the performance of the gasifier can be reviled. Results show that, when sampling the gas upstream of the product gas cooler, it is important to use a particle filter, and to keep the sampling-filter rather clean through pulsing. As shown here, the particles can affect the gas composition even at temperatures of 300-350 °C. Lowering the temperature further could instead cause problems with condensation of tar components and is not a viable option. Instead, one should consider parallel and redundant sampling-filters if the goal is to have continuous sampling. An option is to sample after the main product gas filter instead, but, then vital information about the largest tar components are lost, as these are separated from the gas in the product gas filter or even condense in the cooler. Results also show that the pulsing of the main product gas filter has a strong impact on the tar level in the gas after the main filter, making it difficult to have representative results when sampling from this part of the process. This also makes it complex to evaluate the performance of the primary tar cleaning step as the level of tar in the inlet gas can vary significantly when using a filter setup like the one at GoBiGas.

Sampling the gas after the primary tar cleaning step is rather straight forward as the gas is now poor in large tar components that can foul the sampling system. Even so, there will always be some slip and heating are still required to minimize the risk of affecting the measurements and 200 °C was used in present work for sampling tar. The tar concentration after the RME-scrubber used at GoBiGas is stable and has been leveled out by the scrubber even though the inlet concentration fluctuates. Measurements of the tar at this point gives information about the performance of the gas cleaning rather than the gasifier. It is also worth noticing that the gas is rather dry at this point, as the steam is condensed in the scrubber and it is, therefore required to add steam if one is to reform this gas using a HTR.

The composition of the gas sampled after the primary tar cleaning can be used for a qualitative assessment of the fuel conversion in the gasifier. Different operational cases can conveniently be compared using a specialized Van Krevelen diagram, while the continuous operation can be monitored using the syngas modulus as described in section 2.3.

4.1.2 Start-up

During start up the process is especially sensitive as one has transient behavior in several parts of the process simultaneously. In particular, it can be complex to balance the amount of potassium in the system and there is always a risk to put either too little potassium, with high tar yield as consequence, or too much potassium that clogs the cooler as well. As shown the alkali and particle concentration in the gas can be measured online (section 3.2.5), which would be especially useful during startup. Combined with a correlation between the CH_4 concentration and the level of tar in the gas this can help to avoid clogging of the cooler by both tar and alkali compounds during the transient behavior of the startup.

4.2 PROCESS EVALUATION

To really understand a process and to assess its performance, it is imperative to establish the mass- and energy balance over the process to enable a quantitative evaluation of the process. However, this type of evaluation can be very complex, time-consuming and expensive to perform at a commercial scale biorefinery, such as GoBiGas. Therefore, a method for qualitative evaluation has been established as well, enabling some level of evaluation of the gasifier performance even without the complex mass balance or time-consuming SPA method.

4.2.1 Qualitative Evaluation

By measuring the concentration of the syngas components H_2, CO and CO_2 after the primary gas cleaning step one can qualitatively evaluate the performance of the gasifier by using a specialized Van Krevelen diagram. Figure 37 show 2 examples how this can be utilized, showing the difference in the activation of the bed material at GoBiGas or the difference in the fuel conversion using different bed materials in the Chalmers gasifier. How to interpret the diagrams are further described in Section 2.3 as well as in [15, 16].

To simplify the interpretation of the qualitative evaluation, the syngas modulus is defined to yield an online parameter for qualitative evaluation of the fuel conversion in the gasifier. The largest benefit is that only standard measurements of the H_2, CO and CO_2 are required to reveal the dynamics of the process. A higher value for the syngas modulus corresponds to better conversion into syngas. The definition is given in Section 2.3 and trends are included in Section 3.2.2.

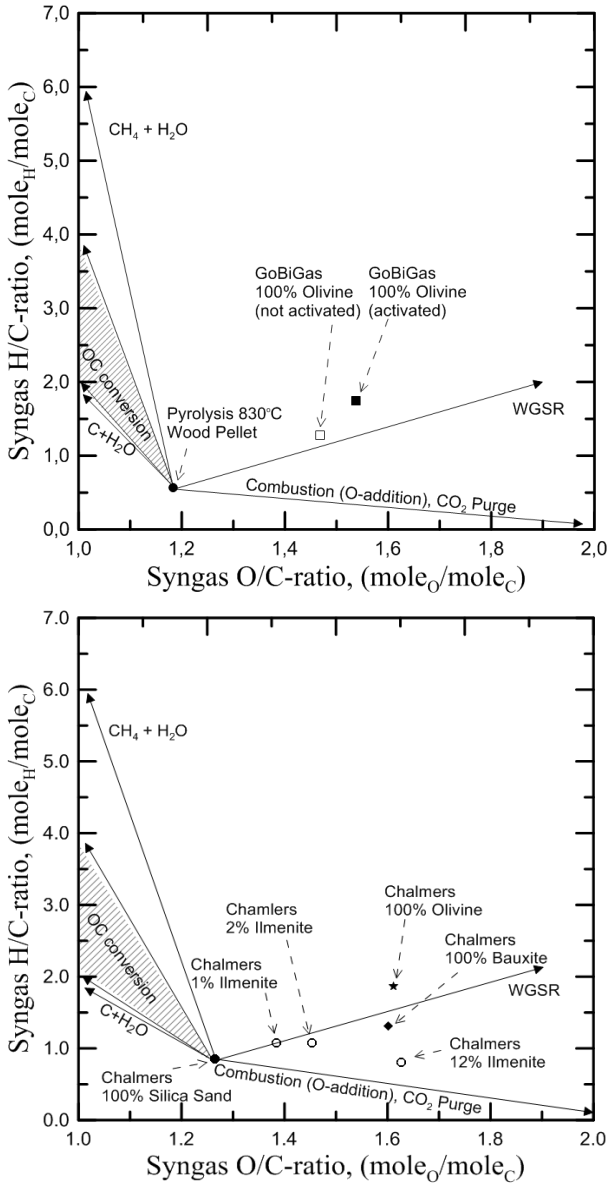


Figure 37: Van Krevelen diagrams specialized for gasification illustrating the difference in the composition of the syngas with different levels of bed material activation (upper), and with the use of different bed materials (lower). From [16]

4.2.2 Quantitative Evaluation

To really quantify how well the fuel is converted in the gasifier further measurements are required. The type of measurements required depends on the level of analysis and thereby system boundary. Figure 38 illustrated the definition applied by A. Alamia *et al.* [2] for the measurement points used to quantify the performance of the GoBiGas-Gasifier. Where the green dotted line indicates the system, boundary established to quantify the performance of the hole DFB-gasifer, here referred to as the cold gas efficiency, η_{CG}. To quantify η_{CG} measurements of the flows, composition temperatures and pressures of points F to L is required. For the product gas, F, it sufficient with a μGC to measure the composition and for the flue gases an FTIR are convenient. Equipment needed for remaining measurements

can be considered standard equipment and are not treated in further detail. These measurements enable evaluation of the performance of the combined gasification and gas cleaning system and are quite straight forward. However, it does not reveal information about the actual fuel conversion and how much of different undesired by-product such as tar that is formed.

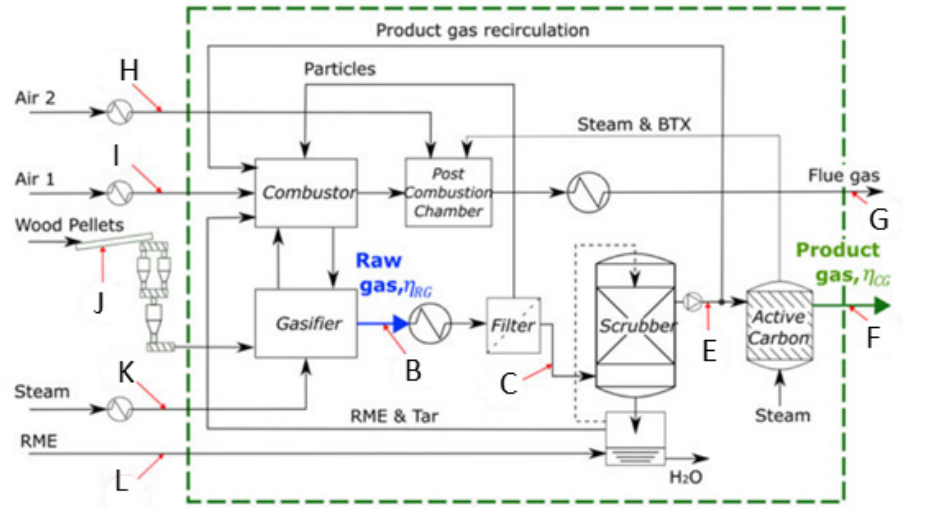


Figure 38: Schematics of a DFB gasifier and the required measurement positions (A to L) required to evaluate the process. From [2]

To increase the understanding of the gasification and the cleaning steps further measurements are required at points B, C and E. Here, the μGC needs to be complimented by tar measurements or with measurements of the composition after reforming the gas in a small high temperature reactor (HTR).

An additional feature used to simplify and improve the evaluation of the performance of the gasifier is the injection of a tracer gas, e.g. Helium. As has previously been shown the yield of each gas composition and total volume flow of product gas can be quantified with high accuracy by injecting a known amount of detector grade He to the gasifier and measure the He concentration in the product gas using a μGC. At GoBiGas up to 100 l_n/min was injected to yield a He concentration that excided 500 ppm in the product gas. Lower concentrations can be problematic to measure with the current method and it can, therefore, be difficult and expensive to apply this method on even larger gasifiers. However, for gasifiers up to about 40 MW the current approach can effectively be applied to accurately establish the mass balance of the gasifier during the commissioning phase.

5 Conclusions

This project has been focused on developing the methodology for monitoring and evaluation of DFB-gasifiers and a new sampling system has successfully been implemented at the GoBiGas-Gasifier. The system has been used in a range of collaborations with other projects to test new measurement devices or gas-treatment equipment, as well as for evaluating the process in detail. The methodology regarding measurements at a commercial scale DFB-gasifier has been summarized and discussed in this report. These are major conclusions from this work:

- There is a clear correlation between the CH_4 concentration and the level of tar in the product gas. This enables monitoring and controlling of the gas quality without complex tar measurements.
- The fuel conversion in the Gasifier can be further evaluated based only on the concentration of H_2, CO and CO_2 by using a specialized Van Krevelen diagram as well as estimating the Syngas modulus which has been formulated as part of this project.
- Concentration of alkali compounds in the product gas can be measured online using a SID and this could be especially useful during start-up to reduce the risk of clogging the cooler with potassium.
- LED-based technology can be used to measure tar online and can be a useful tool for optimization and control of the gas cleaning steps.
- To establish the mass and energy balance of the gasifier the yield of tar should be measured directly using, for instance the SPA method, or indirectly by reforming a slipstream of the gas e.g. in a high temperature reactor.
- Establishing the mass and energy balance can be simplified by injecting Helium as a tracer gas.
- Particles in the product gas that is captured by the main particle filter or by a sampling filter can have a strong impact on the composition of the product gas, which must be considered when designing the main process as well as gas sampling system.

6 Publications and Collaborating Projects

Monitoring the Bed Material Activation in the GoBiGas-Gasifier. Conference paper at the Nordic Flame Days 2015. [15]

SFC – SIGB

Performance of large-scale biomass gasifiers in a biorefinery, a state-of-the-art reference. Published in International Journal of Energy Research. [2]

Efficiency Comparison of Large-Scale Standalone, Centralized, and Distributed Thermochemical Biorefineries. Published in Energy Technology. [19]

Advanced Biofuel Production via Gasification - Lessons Learned from 200 man-years of research activity with Chalmers' research gasifier and the GoBiGas demonstration plant. Submitted to Energy Science & Engineering. [20]

Bark as fuel for dual bed gasification – process evaluation and optimization. To be submitted for publication.

Reformation of Product Gas for Indirect Measurement of the Tar Yield and Gasifier Performance.

Reformation of Product Gas for Indirect Measurement of the Tar Yield and Gasifier Performance. To be submitted for publication.

Coated Heat Exchangers as Self-Cleaning Producer Gas Condensers

Functional surfaces for heat recovery during industrial hydrocarbon-rich gas cooling: can wetting lead to self-cleaning? Submitted to Energy & Environmental Science [21]

New Equipment for Measurement of Alkali and Tar from a Gasifier

Online measurements of alkali metals during start-up and operation of an industrial-scale biomass gasification plant. Accepted for publication in Energy & Fuels. [8]

Char Conversion in Fluidized Bed Indirect Gasification Development of a Methodology for Measurements at the GoBiGas gasifier

Project report published *via* Energiforsk[18]

BioProgGReSs

On-line tar monitoring in an industrial plant – GoBiGas. Planed publication(s)

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21. D. Maggiolo, M.S., H. Thunman, O. Santos, A. Larsson, S. Sasic, H. Ström, *Functional surfaces for heat recovery during industrial hydrocarbon-rich gas cooling: can wetting lead to self-cleaning?* subited to Energy & Environmental Science, 2018.

DEVELOPMENT OF A METHODOLOGY FOR MEASUREMENTS AT THE GOBIGAS-GASIFIER

Genom förgasning i en så kallad dubbel fluidbäddsförgasare kan man producera en energirik gas till exempel från biomassa. Den här gasen kan användas för att producera kraftvärme eller genom syntes konverteras till fordonsbränsle eller andra produkter.

Med målet att producera biometan initierade Göteborg Energi GoBiGas-projektet där man byggde världens första anläggning för produktion av biometan från biomassa i industriell skala. I en första fas demonstrerades tekniken genom en demonstrationsanläggning som hade kapacitet att producera 20 MW biogas.

Målet är att producera ett andra generationens biobränsle i form av biometan. Det görs av restprodukter från skogs- och massaindustrin, exempelvis grot och bark. Tekniken gör det möjligt att producera biobränslen med hög hållbarhet och utsläppen av koldioxidekvivalenter kan reduceras med upp till drygt 80 procent jämfört med bensin och diesel baserat på "well-to-wheel" analys. Tekniken är därmed en viktig del i omställningen till ett mer fossiloberoende samhälle. Här sammanfattas utvecklingen kring mätning och processkontroll vid demonstrationsanläggningen GoBiGas.

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