Gas analysis in gasification of biomass and waste

Guideline report
Document 1

IEA Bioenergy

IEA Bioenergy Task 33

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Coordination
G. Aranda Almansa**,** C. Mourao Vilela, B.J. Vreugdenhil (ECN part of TNO)

Contributions
S. Biollaz, A. Calbry-Muzyka, S. Rodriguez (PSI)
Z. Sárossy , G. Ravenni, A. Fateev (DTU)
R. Seiser (UCSD)
M. Eberhard, T. Kolb (KIT)
N. Heikkinen, M. Reinikainen (VTT)
R.C. Brown, P.A. Johnston (Iowa State University)
P. Nau, K.P. Geigle, P. Kutne (DLR)
I. Işık-Gülsaç, P. Aksoy, Y. Çetin, A. Sarıoğlan (TÜBİTAK Mam)
C. Tsekos, W. de Jong (TU Delft)
F. Benedikt, H. Hofbauer (TU Wien)
L. Waldheim (SFC)
K. Engvall (KTH)
Y. Neubauer (TU Berlin)
I. Funcia, J. Gil, I. del Campo (CENER)
I. Wilson, Z. Khan (U. Glasgow)
D. Gall (Gothenburg University)
A. Gómez-Barea (University of Seville)
F. Schmidt (Umeå University)
L. Lin, M. Strand (Linnaeus University)
A. Anca-Couce, L. von Berg (TU Graz)
A. Larsson (GoBiGas)
J.M. Sánchez Hervás (CIEMAT)
B.F. van Egmond, M. Geusebroek, A. Toonen,
J. Kuipers, M. Cieplik. E.H. Boymans, A.J. Grootjes (ECN part of TNO)
F. Fischer (TUM)
M. Schmid (University of Stuttgart)
J. Maric (Chalmers University of Technology)
F. Defoort, S. Ravel, S. Thiery, M. Balland (CEA)
N. Kienzl, S. Martini, J. Loipersböck (Bioenergy 2020+)
E. Basset, A. Barba (ENGIE Lab CRIGEN)
W. Willeboer (RWE-Essent)
R. Venderbosch (BTG)
D. Carpenter (NREL)
F. Pinto (LNEG)
D. Barisano (ENEA)
M. Baratieri (UNIBZ)
R. Ballesteros (UCLM)

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Abstract

Gasification is generally acknowledged as one of the technologies that will enable the large-scale production of biofuels and chemicals from biomass and waste. One of the main technical challenges associated to the deployment of biomass gasification as a commercial technology is the cleaning and upgrading of the product gas. The contaminants of product gas from biomass/waste gasification include dust, tars, alkali metals, BTX, sulphur-, nitrogen- and chlorine compounds, and heavy metals. Proper measurement of the components and contaminants of the product gas is essential for the monitoring of gasification-based plants (efficiency, product quality, by-products), as well as for the proper design of the downstream gas cleaning train (for example, scrubbers, sorbents, etc.). In practice, a trade-off between reliability, accuracy and cost has to be reached when selecting the proper analysis technique for a specific application. The deployment and implementation of inexpensive yet accurate gas analysis techniques to monitor the fate of gas contaminants might play an important role in the commercialization of biomass and waste gasification processes.

This special report commissioned by the IEA Bioenergy Task 33 group compiles a representative part of the extensive work developed in the last years by relevant actors in the field of gas analysis applied to (biomass and waste) gasification. The approach of this report has been based on the creation of a team of contributing partners who have supplied material to the report. This networking approach has been complemented with a literature review. The report is composed of a set of 2 documents. Document 1 (the present report) describes the available analysis techniques (both commercial and under development) for the measurement of different compounds of interest present in gasification gas. The objective is to help the reader to properly select the analysis technique most suitable to the target compounds and the intended application. Document 1 also describes some examples of application of gas analysis at commercial-, pilot- and research gasification plants, as well as examples of recent and current joint research activities in the field. The information contained in Document 1 is complemented with a book of factsheets on gas analysis techniques in Document 2, and a collection of video blogs which illustrate some of the analysis techniques described in Documents 1 and 2.

This guideline report would like to become a platform for the reinforcement of the network of partners working on the development and application of gas analysis, thus fostering collaboration and exchange of knowledge. As such, this report should become a living document which incorporates in future coming progress and developments in the field.

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Contributing partners

Bioenergy 2020+ (BE2020+)

Centre for Energy, Environmental and Technology Research (CIEMAT)

Chalmers University of Technology

Energy research Centre of the Netherlands, part of The Netherlands Applied Research Organisation (ECN part of TNO)

Free University of Bolzano (UNIBZ)

French Alternative Energies and Atomic Energy Commission (CEA)

Gas Analysis Group (GAW)

German Aerospace Centre (DLR)

Göteborg Energy AB

Gothenburg University

Iowa State University (ISU)

Karlsruhe Institute of Technology (KIT)

Linnaeus University

Luleå Technical University (LTU)

National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA)

National Laboratory of Energy and Geology (LNEG)

National Renewable Energy Centre (CENER)

National Renewable Energy Laboratory (NREL)

Paul Scherrer Institute (PSI)

Research and Innovation Center In Gas and New Energies of ENGIE (ENGIE Lab CRIGEN)

Royal Institute of Technology in Stockholm (KTH)

RWE Essent

Scientific and Technological Research Council of Turkey (TÜBITAK Mam)

Stanford University

Swedish Gasification Centre (SFC)

Technical Research Centre of Finland (VTT)

Technical University of Berlin (TU Berlin)

Technical University of Denmark (DTU)

Technical University Delft (TUD)

Technical University Graz (TUG)

Technical University of Munich (TUM)

Umeå University (UME)

University of California at San Diego (UCSD)

University of Castilla-La Mancha (UCLM)

University of Glasgow

University of Seville

Vienna University of Technology (TU Wien)

Abbreviations

AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectroscopy
AMFIA	Ammonia Flow Injection Analysis
APS	Aerodynamic particle sizer
BFB	Bubbling fluidized bed
BTX	Benzene, toluene, xylenes
CFB	Circulating fluidized bed
CF-WMS	Calibration-free scanned wavelength-modulated spectroscopy
CHP	Combined heat and power
CVAAS	Cold vapor atomic absorption spectrometry
DMA	Differential mobility analyser
DOAS	Differential optical absorption spectroscopy
ELS	Elastic light-scattering
ELIF	Excimer laser-induced fragmentation fluorescence
ELPI	Electrical low-pressure impactor
EPA	United States Environmental Protection Agency
EPC	Electrostatic particle counter
FIA	Flow injection analysis
FID	Flame ionization detector
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GC-AED	Gas chromatography coupled to atomic emission detector
GC-BID	Gas chromatography coupled to barrier ionization discharge
GC-FID	Gas chromatography coupled to flame ionization detector
GC-FPD	Gas chromatography coupled to flame photometric detector
GC-MS	Gas chromatography/mass spectrometry
GC-NCD	Gas chromatography coupled to nitrogen chemiluminescence detector
GC-PDHID	Gas chromatography coupled to pulsed discharge helium ionization detector
GC-PFPD	Gas chromatography coupled to pulsed flame photometric detector
GC-SCD	Gas chromatography coupled to sulphur chemiluminescence detector
HPLC	High-performance liquid chromatography
IC	Ion chromatography

ICP-OES	Inductively coupled plasma atomic emission spectroscopy
IMR-MS	Ion molecular reaction mass spectrometry
IR	Infrared radiation
KF	Karl-Fischer (titration)
LE	Laser extinction
LED	Light emitting diode
LIBS	Laser-induced breakdown spectroscopy
LIF	Laser-induced fluorescence
LII	Laser-induced incandescence
LPI	Low-pressure impactor
MBMS	Molecular beam mass spectrometry
NCD	Nitrogen chemiluminescence detector
NDIR	Non-dispersive infrared sensor
OF-CEAS	Optical-feedback cavity-enhanced absorption spectroscopy
PAH	Polycyclic aromatic hydrocarbons
PID	Photo-ionization detector
RME	Rapeseed methyl ester
SCD	Sulphur chemiluminscence detector
SEM/EDX	Scanning electron microscopy/Energy dispersive X-ray
SID	Surface ionization detector
SPA	Solid phase adsorption
SMPS	Scanning mobility particle sizer
TCD	Thermal conductivity detector
TEOM	Tapered element oscillating microbalance
TLDAS/TDLAS	Tunable laser diode (or diode laser) absorption spectroscopy
TOF-MS	Time-of-flight mass spectrometry
UV	Ultraviolet radiation
UV-VIS	Ultraviolet–visible radiation
VCSEL	Vertical-cavity surface-emitting lasers
VTDMA	Volatility tandem differential mobility analyser
WMS	Wavelength-scanned modulation spectroscopy

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1. Introduction

1.1 MOTIVATION OF THIS WORK

Gasification is a thermochemical process that takes place at high temperatures (in the range of 700-1200°C) in the presence of a gasifying agent (air, O_2, steam, CO_2, or mixtures thereof) in which a carbonaceous solid feedstock such as coal, biomass or waste is converted into a combustible gaseous carrier called product gas or syngas (depending on its composition, which is in turn a function of the type of feedstock, the gasification operating conditions and the type of reactor technology used). The key aspect of gasification is that it transforms the solid fuel into a gaseous fuel (easier to clean and transport and a versatile feedstock) which keeps 70-80% of the chemical energy of the initial fuel [1]. Once upgraded, the product gas can be used for the production of power, heat, fuels, and/or chemicals. Gasification is generally acknowledged as one of the technologies that will enable the large-scale production of biofuels and green chemicals from biomass. Moreover, large-scale biomass gasification processes potentially allow the implementation of carbon capture and storage (bio-CCS), which implies the possibility of achieving negative CO_2 emissions. For these reasons, gasification of biomass and waste is expected to play a central role in the mid-term and long-term low-carbon energy scenarios resulting from the Paris Agreement. In spite of this huge potential, biomass and waste gasification is still under research, development and commercial demonstration, unlike the mature coal and oil gasification processes.

One of the main technical challenges associated to the deployment of biomass gasification as a commercial technology is the cleaning and upgrading of the product gas. The gasification gas contains, besides the main compounds (CO, CO_2, H_2, CH_4, H_2O), traces of impurities and contaminants that need to be removed or converted before using the gas in e.g. a gas engine, a gas turbine, a fuel cell or in synthesis applications. These contaminants include dust, tars, alkali metals such as K and Na, BTX (benzene, toluene, xylenes), sulphur-, nitrogen- and chlorine compounds (e.g. H_2S, COS, NH_3, HCN, HCl), and heavy metals (e.g. Hg, Cd). Although in general clean woody biomass has a low content of sulphur, nitrogen and chlorine, the use of low-cost residual biomass (e.g. agricultural residues, manure, sewage sludge, etc.) or waste (e.g. RDF) as gasification feedstock poses a great challenge in terms of gas cleaning, since the gas contains relatively high concentrations of e.g. NH_3, H_2S and HCl compared to wood gasification [2][3]. Figure 1 displays the typical range of concentrations of contaminants from gasification of biomass and waste, whereas Table 1 gives an overview of the main gas compounds resulting from the thermal conversion of biomass, and their relevance in gasification processes.

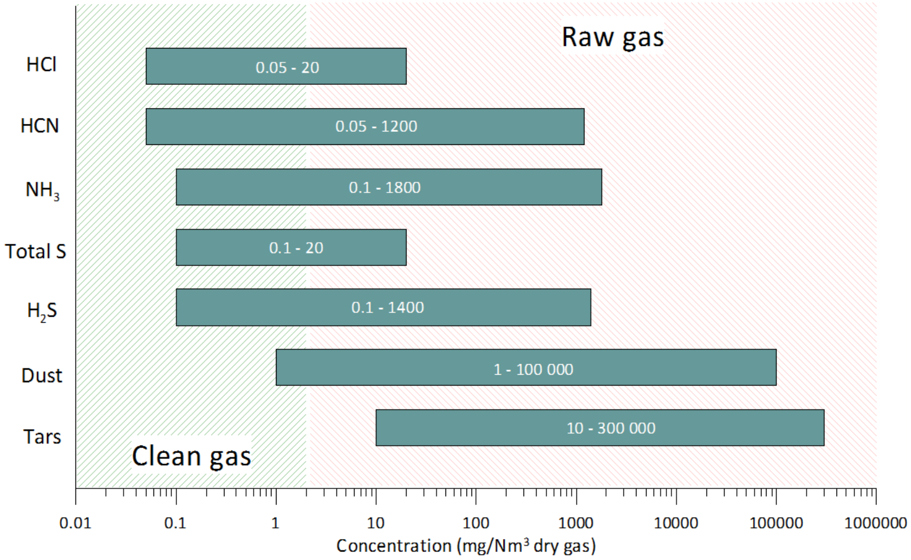


Figure 1. Typical concentrations of contaminants in product gas (adapted from [4]).

Table 1. Gas compounds produced in gasification per biomass element, and relevance on gasification processes [5][6].

Biomass compound	Resulting gas compound	Effect on gasification process
Nitrogen	Mainly NH_3 and HCN Traces of organic N compounds: pyridines, quinolines, etc.	Design of gas cleaning section. Emissions. Deactivation of downstream catalysts.
Sulphur	Mainly H_2S and COS Traces of organic S compounds: thiophenes, mercaptans, etc.	Design of gas cleaning section. Interaction with alkali metals: emissions, deposits, corrosion. Deactivation of downstream catalysts.
Chlorine	Mainly HCl Traces of organic Cl compounds, e.g. CH_3Cl	Decrease of softening temperature of ash. Enhancement mobility of K (→deposition and agglomeration). Emissions, corrosion and ash sintering.
Alkalis (Na, K), Mg, P, Ca	Present in gas as gaseous compounds Deposited as salts	Involved in ash deposition and formation of deposits. Lowering (alkalis, formation of eutectics) or increase (Mg, P, Ca) of ash melting temperatures. Reaction with Si and S: deposition, agglomeration, fouling, corrosion. Ash valorisation/disposal. Ash-melting behaviour (softening and melting temperatures) → deposition, agglomeration, fouling.
Heavy metals	Gas phase	Emissions. Ash disposal costs, ash applications.

With this background, analysis of gas and other contaminants plays (and will keep on playing) a crucial role in the development and commercialization of biomass and waste gasification processes. Proper measurement of the components and contaminants of the product gas is essential for the monitoring of gasification-based plants (efficiency, product quality, by-products), as well as for the proper design of the downstream gas cleaning train (for example, scrubbers, sorbents, etc.). Ideally, gas analysis should be accurate at any expected concentration, reliable, easy to perform, fast (online measurement), and low-cost. In practice, a trade-off must be reached when selecting the proper analysis technique for a specific application.

The importance of gas analysis in gasification is best exemplified by the Gas Analysis Working Group (GAW) in 2011, which aims to optimize the basis of knowledge about sampling, analysis and evaluation of impurities in product gases from gasification, pyrolysis and conditioned syngas. This objective is performed on the basis of exchanging of information and sharing knowledge and experiences [7].

With this background, this report is addressed to an audience dealing with gas analysis applied to biomass- and waste gasification processes, including researchers and plant operators. This work describes the available analysis techniques for the measurement of the different compounds present in gasification gas, thus helping the reader to understand the pros and cons of each option, and thus to properly select the analysis technique most suitable to the target compounds and the intended application of the gas. This report also covers techniques under development and new trends in gas analysis applied to gasification, namely recent progress in online analysis of tar and other gas compounds. Given the fact that this work is the result of a huge collaborative effort intended to reinforce the exchange of knowledge, experiences and contacts from partners on gas analysis have been included whenever possible.

1.2 SCOPE OF THIS REPORT

This special report commissioned by the IEA Bioenergy Task 33 group aims to compile a representative part of the extensive work developed by relevant actors in the field of gas analysis applied to (biomass and waste) gasification. The content of this report includes both existing and under development techniques applied to the measurement of compounds present in product gas, including permanent gases, water, and other trace contaminants (either solid, condensable or gaseous species). The approach of this report has been based on the creation of a team of contributing partners including, but not limited to, the network of the Gas Analysis Working group, which have kindly supplied material to the report. In order to fill in some gaps, this networking approach has been complemented with a literature study.

Some of the techniques described in this report overlap with existing methods applied in related fields (for example, flue gas analysis in combustion or other environmental applications, pyrolysis, coal gasification, biogas production via digestion). In some specific cases (namely the measurement of siloxanes), application in gasification is scarce, thus existing measurement methods applied to biogas have been described instead. Although measurement of particulate matter in product gas has been included in the scope of this report due to its relevance to gasification processes, topics such as analysis of solid fuels, ash and char are not addressed in this document.

Given the broad scope of gas analysis, the overlapping with techniques applied to other thermochemical and biochemical conversion processes, the extensive work developed in the last years, and other project management constraints, it is virtually impossible to cover all the existing knowledge in a single report, thus limitations in the scope of this work are inevitable. This report intends to offer just a brief snapshot of the work and progress on gas analysis applied to biomass- and waste gasification at the moment of the publication. Ideally, this document should become a platform for the reinforcement of the network of partners working on the development and application of gas analysis, thus fostering collaboration and exchange of knowledge. As such, this report should become a living document which incorporates in future coming progress and developments in the field. The gathering of knowledge and experience in gas analysis will hopefully result in the commercial deployment of gasification processes as part of a future bio-based economy.

HOW TO USE THIS MANUAL

This guideline report is composed of a set of 2 documents. Document 1 (the present report) describes the available analysis techniques (both commercial and under development) for the measurement of different compounds present in gasification gas. Complementary information about each measurement technique described in Document 1 can be consulted in the book of factsheets collected in Document 2. In order to further promote research collaboration, Document 2 also includes an overview table containing the contacts of the contributing partners. Finally, as a special appendix to this report, a dedicated channel containing video blogs on gas analysis has been created, which illustrate some of the analysis techniques described in Documents 1 and 2.

IEA Bioenergy Task 33 Youtube channel:
https://www.youtube.com/channel/UCjZQMdEdmaDzNCScS6ckINw/featured

2. Measurement of target compounds of gasification product gas

2.1 INTRODUCTION

This chapter presents an overview of the existing techniques for the measurement of several compounds present in the gas produced during gasification of biomass and waste, classified per target compound. Complementary information about the different analysis techniques described throughout this section can be found in the Factsheets compiled in Document 2.

Throughout this chapter the different measurement techniques have been classified into online and offline methods. In online methods the detector is connected directly to the sampling point, while in offline methods there is a medium between the sampling point and the detector. In the special case that the measurement is performed directly in the line (no sampling point), the method is called in-situ.

2.2 MEASUREMENT OF PERMANENT GASES

2.2.1 General considerations

The most common type of analysis in a gasification process is the measurement of the product gas composition, that is, the concentration of the main gas compounds, such as CO, CO_2, H_2, CH_4, C_2H_x (C_2H_6, C_2H_4, C_2H_2), and larger (C_3-C_5) gaseous hydrocarbons. The determination of the product gas composition allows the calculation of parameters such as the heating value or the Wobbe Index, which are relevant for the application of the gas for heat and power production. Other compounds such as Ar, Ne or He (frequently added in lab-scale applications as tracer gases for the performance of balances around the gasifier or the downstream equipment), as well as O_2 and N_2 will be also considered in this section. The measurement of aromatic gaseous compounds (BTX) will be separately discussed in Section 2.4.

2.2.2 Main gas compounds – CO, CO_2, H_2, CH_4

The detection of main permanent gases in product gas can be performed online using commercially available equipment. Several analysis techniques are available, the most widely used being gas analysers (also called gas monitors), generic name for the equipment that applies a combination of detectors: NDIR, paramagnetic and TCD for online gas analysis; and micro-GC analysers. Online measurements are often complemented with offline methods. Table 2 provides an overview of the different techniques applied for the analysis of the permanent gases among the different contributing partners.

Almost all institutes and plants contributing to this report use at least one type of gas monitor in their measurements of permanent gases. Figure 2 shows as an example the online gas monitor system used at CIEMAT and at ECN part of TNO. Usual sensors used in gas monitor systems include [8]:

- Paramagnetic sensor for the detection of O_2 in the range of 0-25 vol.%
- NDIR (Non-dispersive Infrared Sensor) for the detection of CO, CO_2 and CH_4 in the range of 0-50 vol.%
- TCD (thermal conductivity sensor) for the detection of H_2 in the range of 0-50 vol.%

Table 2. Overview of (online) measurement techniques applied for permanent gases of product gas.

	H_2, CO, CO_2, CH_4, O_2, N_2	C_2H_6, C_2H_4, C_2H_2
BE2020+	Gas analyser/FTIR	FTIR
CEA	Gas analyser / Micro-GC FTIR	Gas analyser / Micro-GC FTIR
Chalmers University CENER UNIBZ	Micro-GC	Micro GC
CIEMAT	Gas analyser / Micro-GC GC-TCD / FTIR	GC-TCD / FTIR
DTU	Gas analyser / FTIR N_2 by far-UV	FTIR/far-UV GC-TCD[1]
ECN part of TNO KIT (REGA) University of Stuttgart	Gas analyser / Micro-GC	Micro-GC
ENEA	Gas analyser / Micro GC GC-TCD	Micro GC / GC-TCD
ENGIE Lab CRIGEN, CEA	OF-CEAS	-
Iowa State University	Micro-GC / GC-TCD	Micro-GC / GC-TCD
KIT (Bioliq)	Quadropol-MS / GC-TCD	-
LNEG	GC-TCD[2] / GC-FID[2]	GC-TCD[2] / GC-FID[2]
DLR Stanford University University of Utah KIT Technical University Darmstadt Umeå University	Laser spectroscopy (TDLAS)	-

	H_2, CO, CO_2, CH_4, O_2, N_2	**C_2H_6, C_2H_4, C_2H_2**
TUD	Gas analyser / Micro GC GC-TCD / FTIR	GC-FID
TUG	Gas analyser / GC-TCD	GC-TCD
TUM	Gas analyser / GC-TCD[3]	GC-FID[3] / GC-TCD[3]
VTT	Gas analyser / Micro GC GC-FID[4] / GC-TCD[4] GC-PDHID[4]	Micro GC / GC-FID[4]

[1] Offline method: sample collected with gas pipettes.
[2] Offline method: sample collected with gas bags.
[3] Offline method: sample collected with gas bags.
[4] Offline method: sample collected with Tedlar gas bags.

CIEMAT

ECN part of TNO

Figure 2. Examples of online gas monitor sets used for online measurement of main product gas compounds.

Micro-GC analysis is also applied by the vast majority of partners involved in gasification. Micro-GCs can perform fast and accurate gas measurements in various process gases, including gasification gases (product gas, syngas, etc.). Due to the possibility of measuring complex mixtures of gases, micro-GC is the most widespread technique used for the measurement of composition of product gas. As an example, at ECN part of TNO the following gases can be measured with micro-GCs: O_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_2H_2, H_2S, COS, benzene and toluene (measurement of xylenes and ethylbenzene has been applied in specific applications), with a frequency of approximately 3-5 minutes (Figure 3).

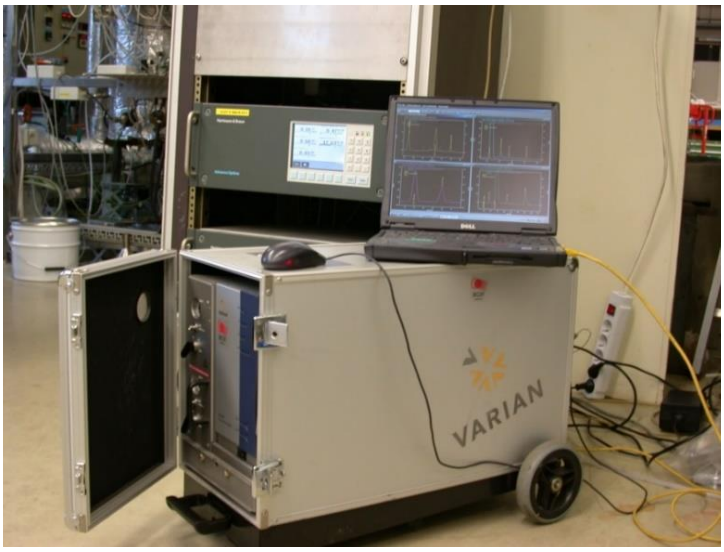


Figure 3. Micro-GC analyser used at ECN part of TNO [9].

As an example, the continuous gas analysers (gas monitors) used at the bioenergy section of ECN part of TNO include NDIR's (non-dispersive infrared detectors) for CO, CO_2, and CH_4; TCD detector for H_2 measurement, and paramagnetic detector for O_2 measurement. The sample gas coming from the pre-sampling system flows through the analysers with a continuous flow of 30-80 L/h regulated by a rotameter. The concentrations are constantly monitored and registered by a PC. The monitors are calibrated with zero gas (pure N_2) and span gas (a certified gas mixture with about the same component concentrations as the process gas to be measured). Although the time resolution is very short (1 s), the detection limit is relatively large (200 ppmv). Another issue encountered when using NDIR detectors is related to the cross sensitivity (interference) between CO and CO_2, which negatively affects the accuracy of the quantification of these gas compounds. Although there are correction algorithms to account for this phenomenon, at ECN part of TNO the cross-sensitivity issues are minimized by calibrating the gas monitor before a test campaign with a gas mixture of composition as close as possible to the expected one. In contrast to gas monitors, micro-GC analysis offers lower time resolution (in the range of 2-7 minutes per analysis), but a relatively lower detection limit (around 10 ppmv), the possibility of measurement of additional gas compounds beyond CO, CO_2, H_2, O_2 and CH_4, and no cross-sensitivity issues.

Although paramagnetic/NDIR/TCD detectors (gas monitor sets) and micro-GC analysers are the most common techniques applied for the measurement of permanent gases, there are other available measurement methods. This is the case of absorption spectroscopy methods (e.g. laser spectroscopy, IR spectroscopy, TDLAS). Spectroscopy methods have several advantages over measurement with GC, namely the possibility of online quantification of a broad number of compounds such as CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, NH_3, HCl and water. FTIR (in combination with GC and other analysers) is applied for example at CIEMAT, DTU, TU Delft and VTT. Gas is sampled automatically and analysed every 1-3 minutes. DTU applies FTIR in situ and (far)-UV absorption spectroscopy online. However, one of the limitations of FTIR spectroscopy is that symmetric diatomic compounds such as H_2, N_2 or O_2 cannot be detected. Moreover, the great absorptivity of CO_2 and H_2O makes the measurement of other compounds challenging. For this reason, spectroscopic analysis is applied complementary to other analysis techniques, thus combining the advantages of both types of analysis [10]. As examples, VTT complements their online measurements (micro GC and gas analysers) with offline methods collected with Tedlar gas bags and further analysed with GC-TCD, GC-FID and GC-PDHID (Pulsed Discharge Helium Ionization Detector), see Figure 4. At DTU, the hydrocarbons analysis is complemented offline with samples collected with gas pipettes and further analysed with a GC-TCD (Figure 5) [11].

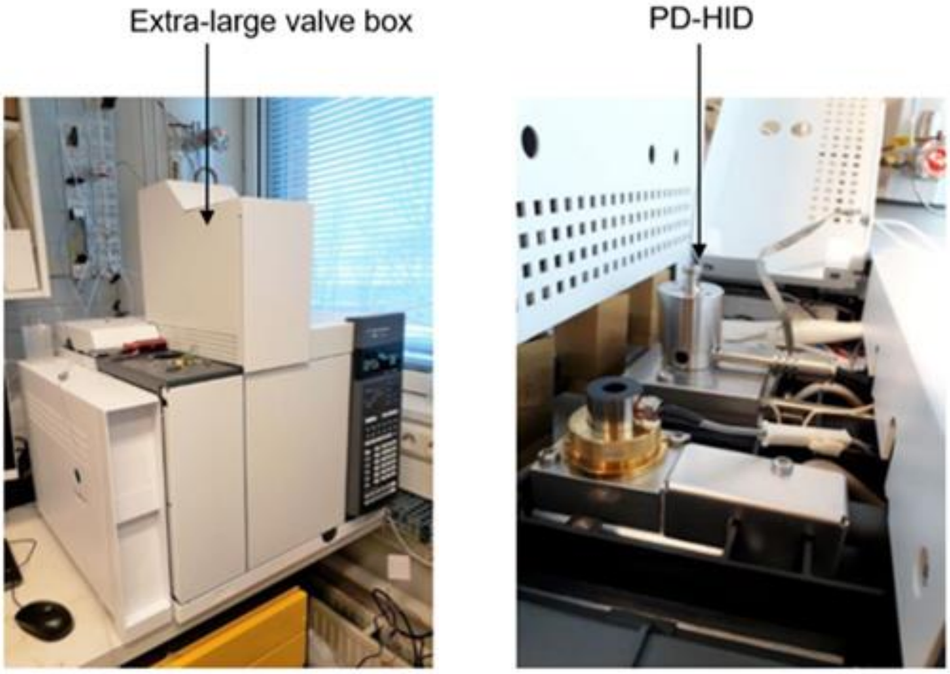


Figure 4. GC-TCD/FID/PDHID unit used at VTT for offline gas analysis [12].

During a comparison between micro-GC and FTIR analysis, researchers from CEA identified a matrix effect of H_2 on CO quantification in FTIR analysis [13]. This matrix effect was not detected on the other gaseous species. Similarly, a matrix effect of H_2O on CO and NH_3 quantification was observed (see more details in Section 2.7.2). The explanation for this effect comes from gas/gas interaction when partial pressures are high, called collisional broadening. From the results of this study, it appears that H_2 and H_2O can induce an important error (close to 50%) on the CO and NH_3 quantification by FTIR, respectively, if they are not taken into account in the calibration method. A mathematical model (similar to the so-called coefficients of cross-correction applied in FTIR gas calibration software), which can be applied in an Excel sheet, was developed and validated in biomass gasification experiments. Further details about this work can be found in Factsheet 10 of Document 2.

Besides FTIR, other spectroscopic methods such as laser absorption (e.g. TDLAS) have also been applied for the online, non-intrusive measurement of CO, CO_2, H_2O and CH_4 [14][15][16][17][18]. OF-CEAS is by CEA and ENGIE Lab CRIGEN (see Sections 3.2.3 and 3.2.8). More details about the application of spectroscopy techniques can be found in Factsheet 1 (and other related factsheets) of Document 2.

Figure 5. Gas sampling with gas pipettes for permanent gases + GC-TCD (offline) analysis at DTU [11].

2.2.3 C_1-C_5 hydrocarbons

Whereas in high-temperature gasification the resulting syngas contains hardly any methane and no larger hydrocarbons, fluidized-bed and fixed-bed gasification processes result in the generation of a product gas which is relatively rich in hydrocarbons. The concentration of hydrocarbons in the gas depends on the operating conditions and the type of gasification feedstock: lower gasification temperatures, lower air/fuel ratios, and the use of waste fuels with respect to biomass favour the production of hydrocarbons in the product gas. Due to their significant contribution to the overall heating value of the product gas, it might be relevant in some applications (for example, the combustion of product gas in boilers, engines or turbines) to know the composition of C_{2+} hydrocarbons (CH_4 can be either measured with NDIR or micro-GC, and C_2 compounds can be detected with micro-GC). GC-FID is a suitable analysis technique for this application.

As an example, at ECN part of TNO, semi-online determination of hydrocarbons is performed by sampling in Tedlar gas bags (2 minutes), and further GC-FID analysis (30 minutes). Factsheet 14 of Document 2 provides further information about the compounds detected. Figure 6 shows an example of application of semi-online GC-FID analysis to the analysis of hydrocarbons, applied at ECN part of TNO. In this case, the fate of C_1-C_5 hydrocarbons over a hydrodesulfurization (HDS) catalyst was evaluated. As can be seen, the HDS catalyst is able to hydrogenate unsaturated hydrocarbons present in the inlet MILENA gas (as well as other organic S and N compounds, see Sections 0 and 2.7.4).

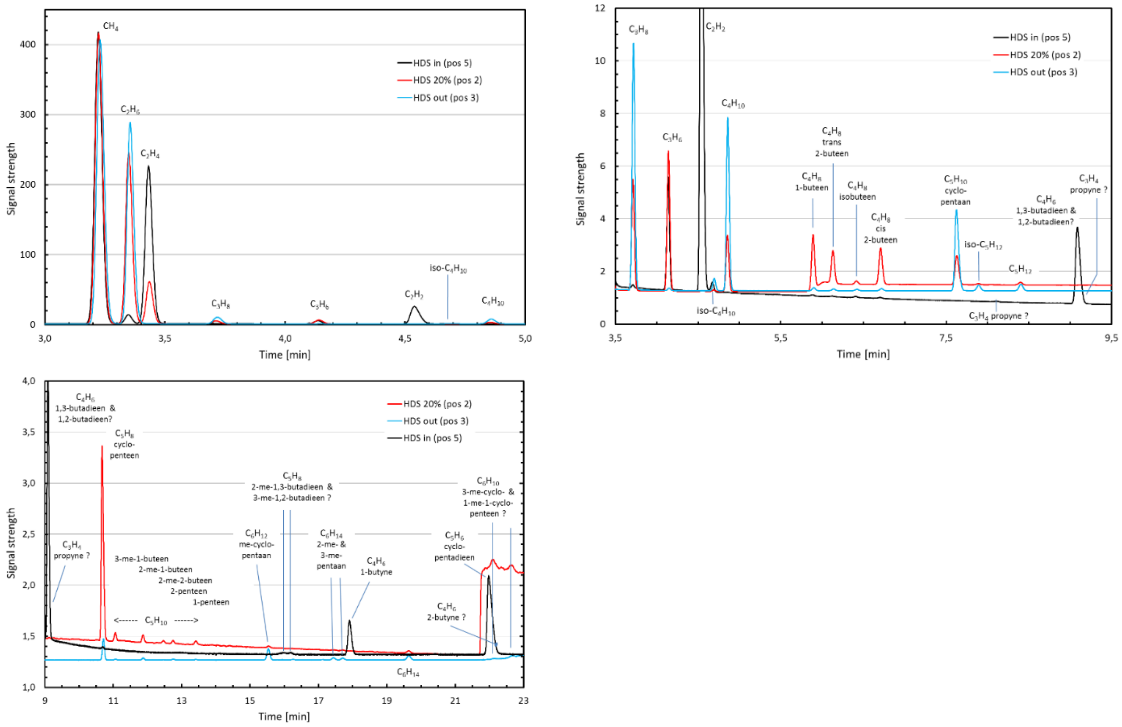


Figure 6. Fate of C_1-C_5 hydrocarbons in HDS reactor using GC-FID analysis. Gas analysis positions: inlet HDS reactor (black line); 20% within the HDS catalyst (red line); outlet of HDS reactor (blue line). Figures courtesy of ECN part of TNO.

2.2.4 Gas conditioning for analysis

Before the product gas is entering the gas analysis equipment, it is very important to ensure that it is free from water, condensable tars, dust and aerosols, which could damage the expensive analysers and give inaccurate measurements. The application of gas conditioning systems is thus necessary. In this section, we describe several examples of gas pre-conditioning systems.

a) Pre-sampling system at ECN part of TNO

In normal conditions (product gas relatively clean, for example after tar removal), the sampled gas is first cooled to a dew point of 5°C by a Peltier cooler. The formed condensate is constantly removed by a peristaltic pump. After the cooler, the gas is filtered by an aerosol filter and pumped to the continuous flow analysers or micro-GCs. When raw, tar-loaded product gas needs to be analysed, an additional special pre-sampling system must be placed in front of the above mentioned normal pre-sampling system. This special pre-sampling system consists of a vessel cooled to 5°C which contains a filter thimble of glass fibre (Figure 7). [9]. The raw hot gas (at temperatures above 300°C) enters the cooled vessel directly into the filter thimble, where the heavy tar components condense out.

Figure 7. Condensation pot of gas pre-sampling system used at ECN part of TNO [9].

b) Dilution system at VTT

For the proper implementation of analysis in raw product gas, VTT has developed (patented technology) a dilution system [19][20]. The dilution equipment is heated at 300°C to avoid tar condensation. Nitrogen is used as dilution gas, whereas sulphur hexafluoride (SF_6) is applied as tracer gas for monitoring the dilution factor. Once that the product gas has been diluted, measurement of particulate matter using an ELPI unit, and online gas and tar analysis using GC and FTIR, can be applied. Figure 8 schematically plots the location of the gas dilution system and the different analysers applied downstream, whereas Figure 9 shows pictures of the implementation of the dilution system.

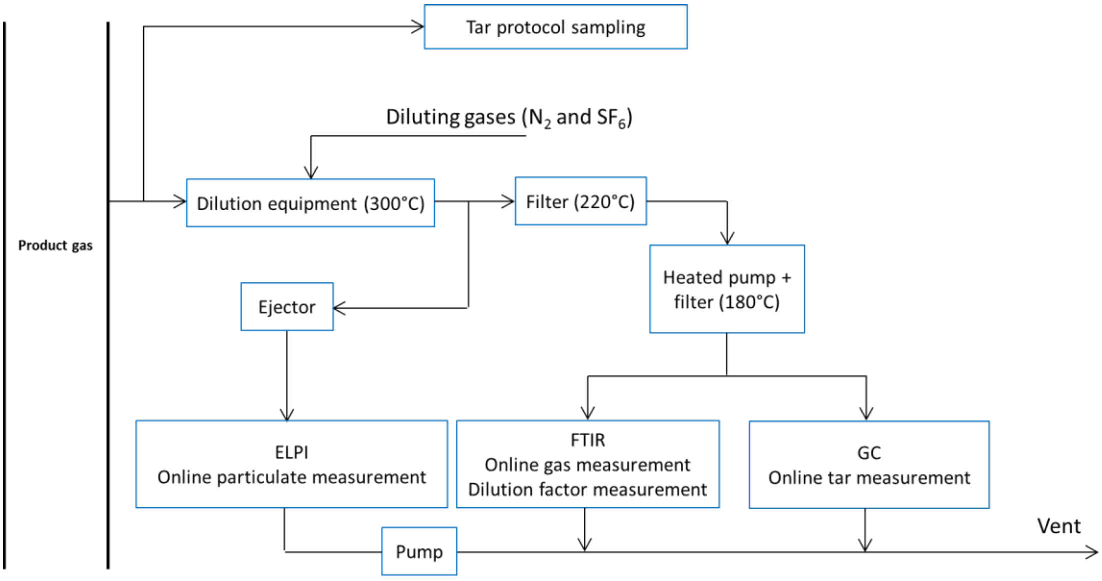
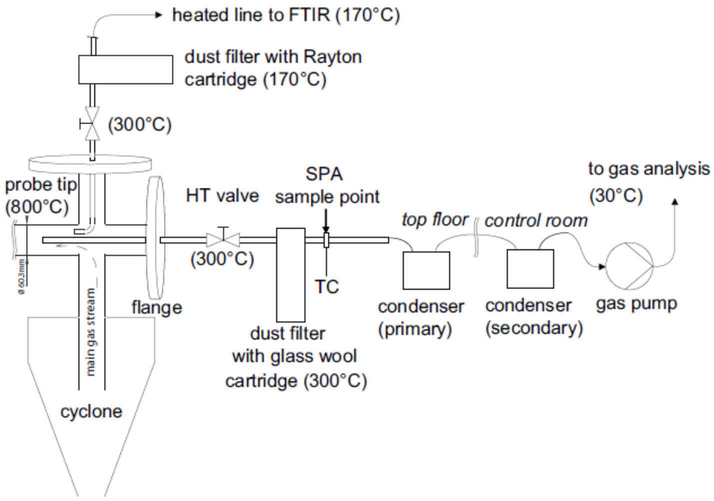


Figure 8. Schematic layout of gas conditioning and analysis equipment for online measurement of particles, gas and tar at VTT [19].

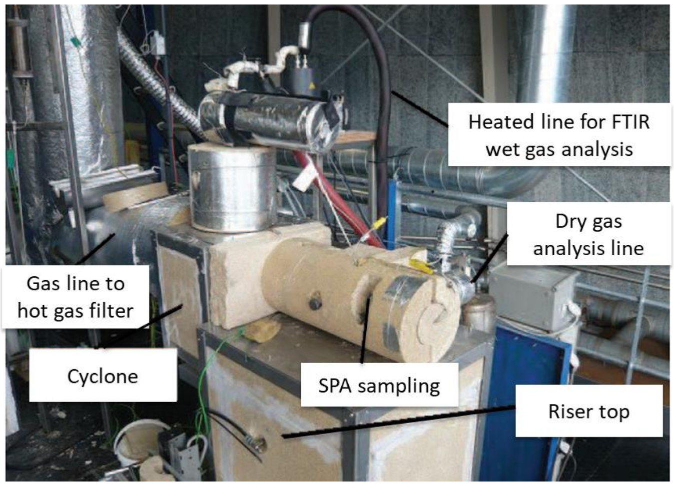
Figure 9. Dilution sampling probe applied at VTT [19].

c) Gas conditioning at TU Delft

The gas analysis sampling line applied at the circulating fluidized bed setup at Technical University Delft is schematically depicted in Figure 10. The lines as well as the particle filters are electrically heat-traced at 300°C. After removal of particles in a filter, the gas enters a primary condenser for the removal of heavy tars and water, and then a secondary condenser. After the condensers, water is removed in 2 impingers filled with silica gel. The conditioned gas then enters the gas analysers (online gas monitors, micro-GC and FTIR). Wet product gas can be also analysed using FTIR. In this case, the gas line is heated to 170°C to avoid water condensation [21].



(a)



(b)

Figure 10. Schematic layout (a) and picture (b) of gas conditioning system for gas analysis applied at TU Delft [21].

d) Gas conditioning at Iowa State University

The gas sampling system applied at Iowa State University consists of a quartz thimble filter for removing char, a pressure cooker heated to approximately 105°C to remove tars, a series of impingers to collect trace gas components and a desiccate canister for water removal. The clean product gas is then analysed by micro-GC or a dual GC-TCD for permanent and non-condensable gases. Figure 11 displays schematically the gas conditioning and sampling system [22]. It is composed of (1) 53 mm inner-diameter raw syngas pipeline, (2) isokinetic sampling probe located at sampling port A, (3) 8 mm I.D. stainless steel tubing heat traced to 450°C, (4) quartz thimble filter inside tube furnace at 450°C, (5) 8mm I.D. tubing at 450°C, (6) tar collection pressure cooker at 100–115°C, (7) stainless steel needle valve and 8mm I.D. tubing heated to 120°C, (8) tubing tee and septum for SPME sampling of light tars, (9) two 500 mL glass impingers in a water–ice bath for water collection and wet chemical measurements of ammonia and hydrogen cyanide, (10) desiccate canister for final water aerosol removal, (11) diaphragm vacuum pump, (12) rotameter with integral control valve, (13) micro-GC, (14) drum-type total flow gas meter, and (15) outlet to exhaust. More information about the facilities and the gas analysis applied at Iowa State University can be found in Section 3.2.15.

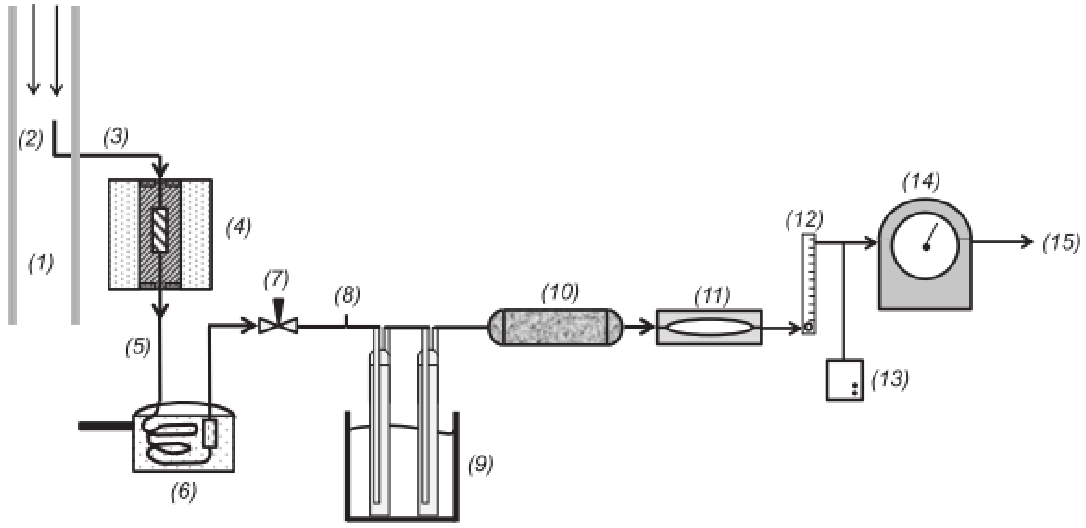


Figure 11. Gas conditioning and gas sampling system used at Iowa State University [22].

2.3 MEASUREMENT OF WATER CONTENT

The water content in product gas depends on several factors, including the properties of the initial biomass feedstock, the gasification operating conditions (pressure, temperature) and the gasification technology. Raw product gas can contain up to ca. 40 vol.% water (e.g. indirect gasification). Moreover, downstream gas upgrading often involves the removal of water condensate and the addition of steam for catalytic processing (e.g. steam reforming, methanation). Therefore, the measurement of water along the gasification, gas upgrading, and synthesis units can provide valuable information about the performance of the process, for example on the efficiency of biomass pre-treatment, the activation of the bed material in the gasifier (relevant aspect in fluidised bed gasification), the efficiency of gas cooling, the control of the inlet conditions at catalytic reactors to avoid carbon formation, etc. Since the operating conditions in a gasification plant can vary, online measurement of water is a desirable requirement in gasification plants for synthesis applications in order to have a quick track on the mass balances and the plant performance.

The water content in product gas can have some negative effects on gas analysis, as discussed by Kleinhappl [23]. These effects include dilution of solvents, phase separation, slip of non-polar fractions during sampling, layering on SPA sorbent columns (thus reducing tar capture), ice formation, baseline instabilities in GC-FID analysers, or discrimination during evaporation in GC injectors. Kleinhappl proposes several measures or strategies to deal with the water content in the gas to mitigate these issues [23].

Water quantification can be performed offline, (semi-) online, and in real time [23]:

- Offline sampling of water can be done by gravimetric quantification, by adsorption on a solid phase (desiccants such as silica gel for example), or by absorption in liquid phase (solvent like for example 2-propanol or methanol). In general, offline sampling is low-cost, but it involves manual procedures which suffer from problems like co-adsorption, tar deposits, and slip of non-polar compounds.

- Online and semi-online sampling can be performed by chromatographic separation. Problems of this type of sampling includes co-adsorption on the columns, and conditioning (maintenance) of transfer lines and columns.

- Real-time sampling methods include hygrometers, acoustic measurement, and spectrometry methods (NDIR detector, FTIR). Limitations of these techniques are for example interference from dust and tar deposits, dependence of main gas components in acoustic measurements, and band overlapping (IR spectrometry). Moreover, real-time sampling involves high cost.

The most straightforward (and least costly) option for water measurement is a gravimetric quantification of condensation of water in the gas analysis set (see for example, the pre-sampling system described in Section 2.2.4 (a)). In this case, the water content is then calculated as the mass of water collected during a certain period within a certain total volume of gas (determined by a gas meter) at specific conditions of pressure and temperature. This method is applied in duration tests at ECN part of TNO. Technical University of Denmark applies a self-designed water and tar condensation setup that can be used for the determination of gravimetric tar and water in a simple way, without the need for solvents or advanced sampling systems. Although easy to implement, gravimetric determination is an offline measurement which requires relatively long sampling times, and it can moreover lead to inaccuracies due to the simultaneous condensation of organic compounds (tars). Gravimetric determination of water does not allow tracking of fast variations in the gasification process, since it can only provide an average value during the gas sampling period.

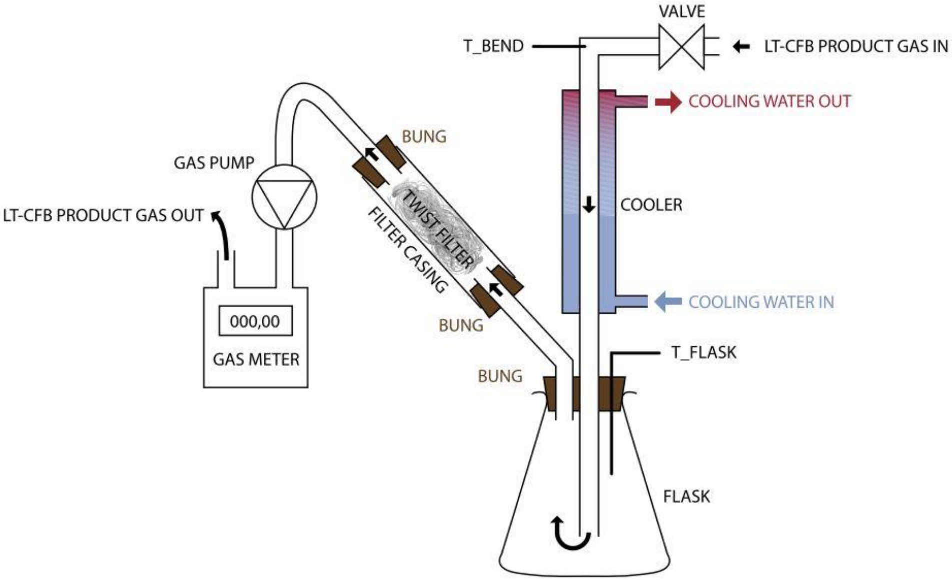


Figure 12. Tar and water condensation setup applied by DTU [24].

Another widespread analysis option for offline quantification of water is the use of Karl-Fischer (KF) titration applied to a sampling solution [25][26]. This is a convenient option in case tar guideline analysis is applied for tar measurement, since the same 2-propanol solution from the tar sampling in the impinger train can be applied for the determination of water content via KF titration. Please refer to Factsheet 20 on KF titration in Document 2 for more information).

The use of P_2O_5 sorbents is another alternative available for the (offline) determination of water in the gas. P_2O_5 is used as desiccant, and this property can be applied for the measurement of water. The application of P_2O_5 is similar to SPA sampling (see Section 2.5.2). In this case, a cartridge containing 1.5 g P_2O_5 is placed in a syringe and connected to the same apparatus (automated gas pump) as in tar sampling using SPA [27]. Although this is still an offline method, it allows faster determination of water content compared to conventional gravimetric determination, in an equivalent way to SPA compared with tar guideline in the case of tar measurement. Gas sampling takes approximately 2-3 minutes, thus allowing better tracking of variations in the gasification process, and no further analysis is required. The increase in weight in the cartridge upon sampling is due to the absorption of water by the P_2O_5, thus the water content can easily be calculated from the weight difference of the cartridge before and after the sampling. Similar considerations in gas sampling as described in the SPA method (see Factsheet 37 in Document 2) apply for this method. The main limitation of this method is that water determination with P_2O_5 is only suitable for tar-free gas, since tars contained in the gas can also be trapped in the cartridge, thus negatively affecting the accuracy of the measurement (Figure 13). Moreover, although faster than tar guideline or gravimetric determination, it is not an online method, and thus fast variations in the gasification process cannot be followed.

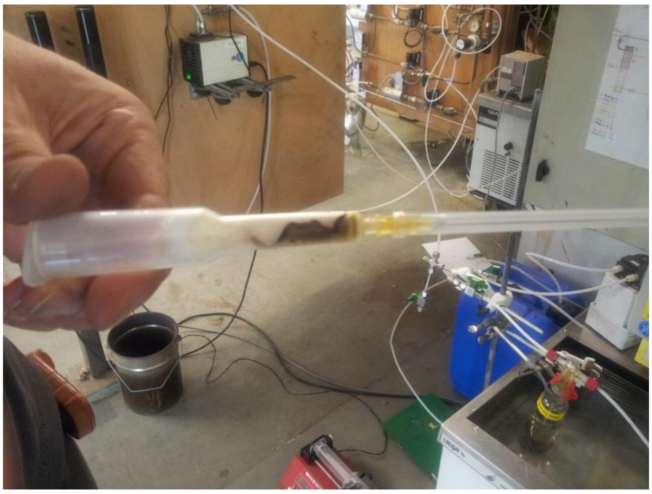


Figure 13. Measurement of water using P_2O_5 – effect of sampling tar-containing gas. Picture courtesy of ECN part of TNO.

Online quantification of water content is also possible. For example, University of Stuttgart applies a hygrometer [28][29] for the continuous monitoring of water content. Other available techniques include GC-MS analysis and spectroscopy methods such as FTIR, TDLAS [14][15][16][17][30], or OF-CEAS. More information about the application of FTIR, TDLAS and OF-CEAS analysis can be found in Factsheets 10, 43 and 31 of Document 2, respectively.

2.4 BTX (BENZENE, TOLUENE AND XYLENES)

2.4.1 General considerations

Although not present in the syngas from high-temperature gasification, low- and medium-temperature gasification processes (in practice, most of the commercial technologies currently available for biomass and waste gasification) produces significant concentrations of BTX. For example, product gas from indirect gasification of wood can contain approximately 5000– 10000 ppmv benzene (dry basis). Toluene concentrations are around 10 times lower than those of benzene, and xylenes are scarcely present in the gas. These concentrations boost if plastic-containing waste is used as gasification feedstock (where concentrations up to 2.5 vol.% benzene and 2000 ppmv toluene can be encountered). In this latter case, gasification can be considered as up-recycling process which breaks up the plastic feedstock into monomers which can be then further converted again into fuels and chemicals.

If the gasification product gas is used as feedstock for synthesis of fuels, BTX need to be either physically removed from the gas or catalytically converted, since these compounds are responsible for catalyst deactivation (coke precursors). For example, in the GoBiGas bio-SNG plant (Sweden), BTX are removed from the gas in an active carbon bed. In the ESME methanation process developed by ECN part of TNO, BTX are converted into methane in a pre-reformer, thus adding to the overall energy efficiency. However, BTX can be used as feedstock for a broad variety of high-value chemicals and materials, and thus the harvesting of bio-BTX from the gasification product gas is considered as an attractive option for the business case of gasification processes [31]. In all the cases described (either removal/conversion or recovery of BTX from gas), the measurement of benzene, toluene and xylene is a relevant issue.

2.4.2 Measurement of BTX

In this report the measurement of light aromatics BTX is described as a separate category from tar measurement and other permanent gases. However, BTX can be detected either as part of the set of permanent gases or as tar compound. The analysis techniques applied by various partners for the measurement of BTX are summarized in Table 3. The most straightforward option for BTX detection is the use of a micro-GC with a TCD detector (as an example, using a CP-wax-52CB1 column at ECN part of TNO). Micro-GC analysis allows the online measurement of BTX (analyses every approximately 4-5 minutes). However, it has also some disadvantages: firstly, the relatively high detection limits (higher than 10 ppmv). The accuracy of the quantification can also be jeopardized by the fact that a fraction of the BTX contained in the gas might be removed in the pre-sampling system of the equipment, where the gas is cooled down to remove water and condensables to protect the GC columns (see Section 2.2.4 (a)), thus the maintenance of the pre-sampling system can affect the measured BTX concentration. On top of that, BTX are sticky compounds that adhere to the walls of the gas analysis lines, which further affects negatively to the accuracy of the measurement (for example, when performing analysis in a just cleaned analysis line, or if the position of gas analysis is switched from "dirty" to "clean" positions). In this case, a good practice to mitigate the latter issue might consist of the use of different gas analysis sets for "clean" (e.g. after a sorbent or catalytic bed) and "not so clean" (e.g. before sorbent bed) positions. This approach is applied for example at ECN part of TNO in duration tests, where 3 different gas analysis sets are implemented: one for product gas after the gasifier and the tar removal unit (dirtiest gas); a second set with analysis positions around the HDS and ZnO reactors (gas without tars, but still containing BTX); and a third analysis set with analysis positions after the pre-reformer and methanation reactors (gas free from BTX and sulphur compounds).

Table 3. Overview of techniques applied for measurement of BTX.

	Method	Sampling	Detector
CEA	Offline	Tar protocol SPA	GC-FID / GC-MS
	Online	Micro-GC IMR-MS	GC-TCD GC-MS
CENER	Offline	Tar guideline	GC-MS
Chalmers	Offline	SPA	GC-FID
CIEMAT	Online	-	FTIR / GC-FID-MS

	Method	Sampling	Detector
DTU	Offline/online	-	GC-MS/UV
ECN part of TNO	Online	Micro-GC	Micro-GC (TCD)
	Offline	Tar guideline	GC-FID/GC-MS
ENEA	Offline	Tar guideline	GC-FID
Goteborg Energi	Online	-	Micro-GC (TCD)
Iowa State	Offline	-	GC-FID
TU Graz	Offline	Tar guideline	GC-FID
TUM	Offline	SPA	
UNIBZ	Offline	Tar guideline	
University of Stuttgart	Online	-	FTIR
	Offline	Tar Protocol	GC-MS
VTT	Offline	Tar protocol	GC-FID / GC-PDHID
	Online	-	GC-FID

BTX can also be measured using the same sampling and analysis methods as for tar determination. The application of the tar guideline (see Section 2.5.2) provides accurate quantification of light aromatics. However, it is an offline analysis, which is also time consuming. The tar sampling time can be considerably reduced if SPA sampling is applied instead of the tar guideline. However, in this case it is necessary to take into account that BTX cannot be quantitatively measured using conventional NH_2 sorbent material [32], since these light aromatic compounds do not completely adsorb in the cartridge. However, there are options to improve the determination of BTX using SPA sampling, namely by the addition of extra active carbon sorbent column placed in series with the NH_2 column [33].

VTT applies for the measurement of BTX and light tars an online GC-FID based on the dilution sampling patented by VTT. Figure 14 shows the results of the comparison of the VTT tar online system with the tar guideline reference, where it can be seen that the results are in general comparable in the case of benzene and naphthalene, whereas more significant deviation can be observed in the measurement of toluene and tars larger than naphthalene. Technical University of Denmark (DTU) applies spectroscopy methods for the online determination of light tars, such as BTX for example. BTX can be measured in the 170-190 nm region using far-UV spectroscopy. A Petersen column coupled to GC-MS analysis can be used for the calibration of the reference far-UV/UV absorption cross-section measurements for selected BTX compounds, which is needed for real data analysis [11][34]. Further details about the application of absorption spectroscopy to tar analysis by DTU can be found in Section 3.2.6. The French Alternative Energies and Atomic Energy Commission (CEA) applies the tar protocol, micro-GC (GC-TCD), SPA and IMR-MS [35][36].

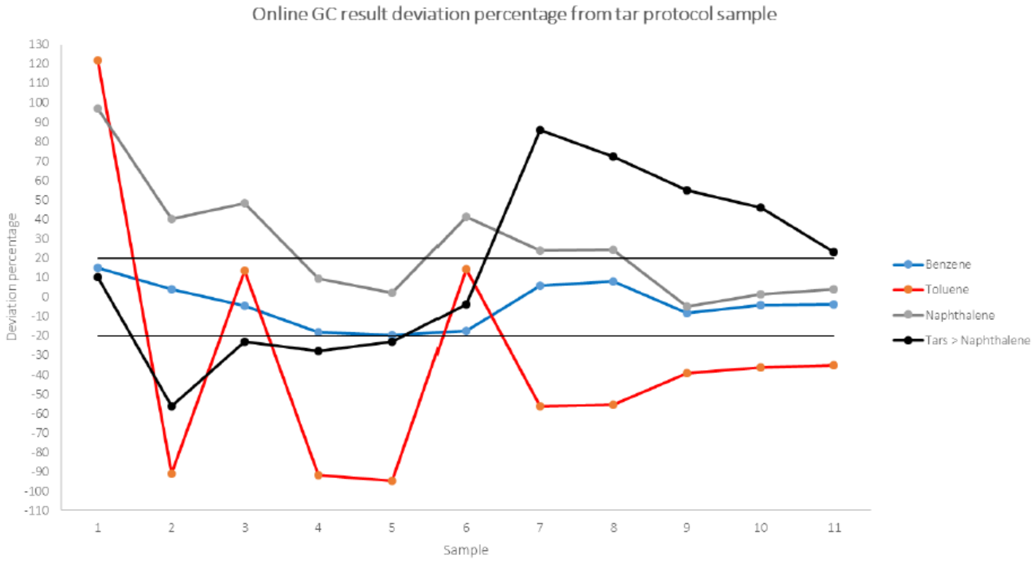


Figure 14. Comparison of results of the online measurement of tar developed by VTT with the tar guideline method [19].

2.5 TAR COMPOUNDS

2.5.1 General considerations

According to the CEN/TS 15439, tar is defined as the hydrocarbons larger than benzene [37]. The generic term “tars” refers to a group of hydrocarbons present in product gas that can condense at relevant working temperatures in gasification-based processes, thus leading to problems of fouling and unwanted plant stops. The resulting condensed tar mixture contains a large number of compounds. Due to the large technical challenge that tar management (for example, removal, conversion, wastewater treatment) poses on gasification plants [38], there has been an extensive amount of research devoted to the development of methods for the accurate measurement of tar content and composition. For this reason, the literature in this field is abundant (see for example [39]).

Table 4. Overview of steps comprising tar measurement, and available techniques for each step (based on [40]).

Method	**Sampling (capture)**	**Sample conditioning**	**Sample analysis**
Offline	• Condensation • Adsorption (SPA) • Cold trapping + absorption /dissolving (tar guideline)	• Dilution • Spiking with internal standards • Desorption (thermal, or with solvents) • Solvent evaporation	• Gas chromatography: GC-FID, GC-MS • Liquid chromatography: HPLC • Gravimetric
Online	-	-	• Molecule ionization: PID, FID • Emission spectroscopy: LIF, UV • Absorption spectroscopy: (FT)IR • Mass-selective detection: MBMS, TOF-MS, ion-trap-MS, quadrupole-MS, IMR-MS

Tar measurement techniques can be firstly classified as online and offline methods [19]. In online methods a detector is directly connected to the sampling point while in offline methods the sample must be captured and brought into an analytical laboratory. The overall process of offline measurement of tars comprises in turn several steps: the sampling (capture) of tars, the conditioning of the resulting sample, and finally the analysis of the sample. Table 4 shows an overview of the possible techniques available for each step, the combination of which result in several tar measurement methods that will be described in detail later in this section.

2.5.2 Offline tar analysis methods

The most important offline tar measurement methods applied to tar measurement are the tar guideline (or tar protocol) and the SPA analysis:

- The tar guideline protocol (CEN/TS 15439)[37], consisting on cold trapping of tar compounds in a series of impinger bottles filled with a solvent (Figure 15), has been developed by a number of European institutions [41][42]. Even though it is a reliable method for the quantification of both light and heavy tar compounds, the guideline method is difficult to implement, requires a long sampling time to quantify tar at low concentration ranges, is a labour intensive (thus costly) method, and is not well adapted for very low tar concentration (< 1 mg/Nm^3) [43]. Moreover, the handling of solvents might pose a safety risk in gasification plants. Further details about the practical implementation of the tar guideline can be found in Factsheet 41 in Document 2.

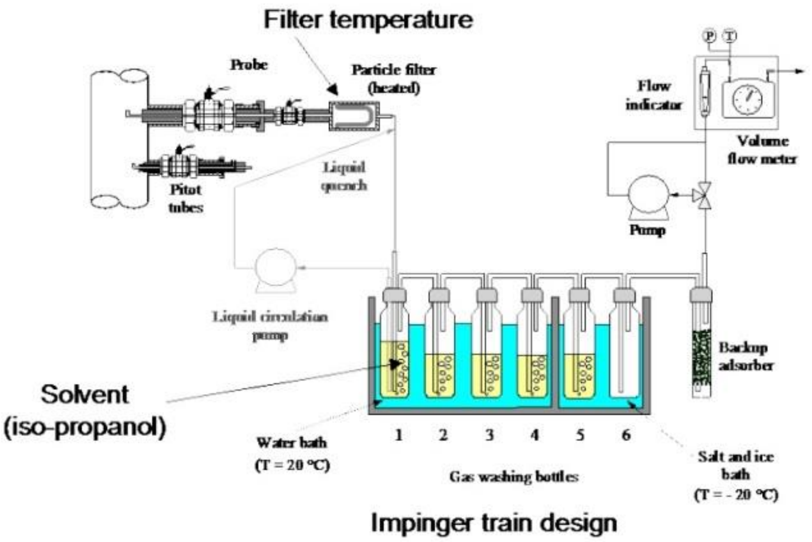
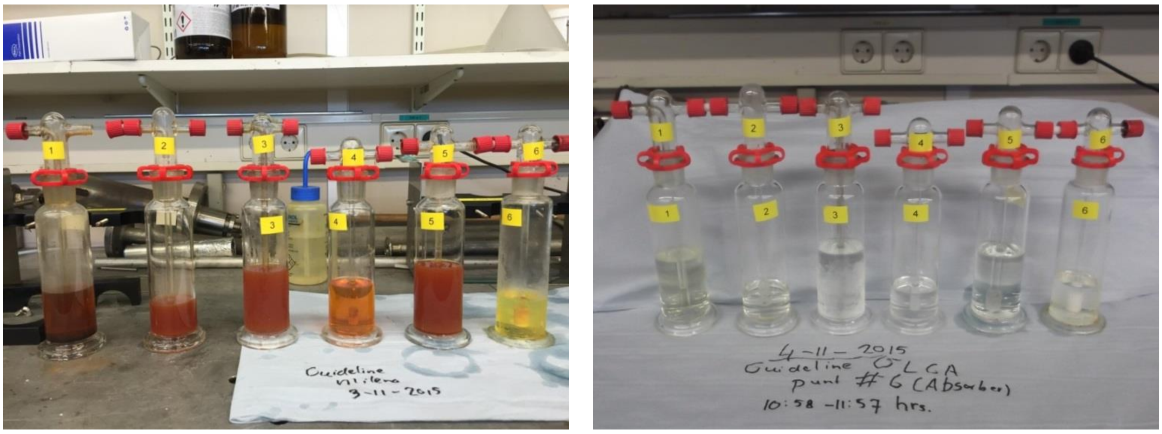


Figure 15. Schematic of tar sampling train according to the tar guideline [37][42].



(a) (b)

Figure 16. Impingers after tar guideline sampling: (a) raw MILENA product gas; (b) Gas after OLGA tar removal. Picture courtesy of ECN part of TNO.

The Solid Phase Adsorption (SPA) method, originally developed by KTH [44], consists of the sampling of gas through a sorbent material (amino-phase NH_2 [32] being the most widely used) which captures the tar compounds. Afterwards, the tar-loaded SPA sorbent is extracted using different solvents (for example, aromatic and phenolic fractions are separately extracted by KTH and Chalmers University of Technology), and analysed using gas chromatography (usually GC-MS and/or GC-FID) [45]. The main differences between the tar guideline and the SPA method are summarized in Table 5. The SPA method offers the advantages of being fast, convenient, simpler in use and maintenance, with good reproducibility and suitable for low tar concentration [46]. The SPA method can detect Polycyclic Aromatic Hydrocarbons (PAHs) in a range of 104-300 g/mol (i.e. styrene to coronene) with a reproducibility within 10% for most compounds [47][48], and is able to provide comparable results to the CEN/TS procedure for non-volatile tar compounds [42]. Furthermore, the uncertainty associated to the tar sampling with SPA is claimed to be lower than the uncertainty associated to the tar sampling with impinger bottles [49]. However, since it is an offline method, the total analysis takes several hours, and most importantly, light compounds such as benzene and toluene are not completely adsorbed [33][39][42][43][44][47][48]. Further details about the SPA method can be found in Factsheet 37 of Document 2.

KTH is also developing Solid Phase Micro-Extraction method (SPME) as an improvement over SPA for the analysis of tar compounds in product gas. SPME is suitable for the analysis of trace amounts of tars (clean syngas) due to the lower detection limits compared to SPA analysis [50]. Moreover, SPME is a solvent-free method: once the tar compounds are adsorbed onto the PDMS phase, the fibre is placed in the GC injector, where the analytes are directly desorbed (thus, no solvent extraction step is needed as in SPA analysis). Further information about the SPME method can be found in Factsheet 38 of Document 2.

Table 5. Comparison of features of the main offline tar analysis methods.

	Tar guideline (CEN/TS 15439)	SPA sampling
Principle	Cold trapping in liquid solvent (2-propanol)	Adsorption in a solid phase (amino-based, active carbon, etc.)
Sampling time	30 min – 1 h	1- 2 min
Desorption time	-	1 hour
Analysis time	2 hours	2 hours
Application	Mainly lab-scale	Suitable for commercial environment (complying with strict plant safety regulations)

Table 6 shows as an example the measurement range and uncertainty of different analytical techniques applied to the speciation of tar compounds at ECN part of TNO.

Table 6. Analysis ranges and uncertainty of analysis of tar compounds per measurement method at ECN part of TNO.

Compound	Analysis technique	Measurement range	Measurement uncertainty
16 PAH EPA	HPLC	1-100 µg/kg	10-15%
	GC-FID	50 -500 µg/kg	10%
	GC-MS	1-100 µg/kg	10%
16 PAH EPA + 20 most abundant tar compounds	GC-FID	5 – 500 mg/m^3 gas	5– 10%

KTH is developing Solid Phase Micro-Extraction method (SPME) as an improvement over SPA for the analysis of tar compounds in product gas. SPME is suitable for the analysis of trace amounts of tars (clean syngas) due to the lower detection limits compared to SPA analysis [50]. Moreover, SPME is a solvent-free method: once the tar compounds are adsorbed onto the PDMS phase, the fibre is placed in the GC injector, where the analytes are directly desorbed (thus, no solvent extraction step is needed as in SPA analysis). Further information about the SPME method can be found in Factsheet 38 of Document 2.

In addition to the more conventional analysis of tar compounds using GC-MS or GC-FID, other research groups have applied other techniques for the analysis of tars. For example, Hernández et al. [51] developed an analysis method based on high-performance liquid chromatography (HPLC) for the determination of BTEX, PAHs (list of 16 EPA compounds) and heterocyclic tar compounds (phenol and pyridine). For that, 2 different analytical methods, each one with a different chromatographic column, a Supelcosil LC-PAH, 5 μm for detection of PAHs and BTEX, and a Supelcosil LC8, 3 μm, 150 x 4.6 mm, for detection of phenol and pyridine. The detection limit of the HPLC equipment was 0.3 μg/mL.

Tar can be measured gravimetrically using alternative setups. The condensation setup developed by Technical University of Denmark for measurement of water and tar content was already described in Section 2.3. Moreover, Technical University of Denmark applies the Petersen column (see Factsheet 34 in Document 2) for tar sampling. Based on the Petersen column, Technical University Graz developed the Compact Trapping System (described in Factsheet 34 of Document 2), which claims to be more robust and compact than the Petersen column [52]. This setup has been applied by TU Graz, Bioenergy2020+ and the company Cleanstgas GmbH. Iowa State University developed a "pressure cooker" setup consisting of a dry condenser system, as explained in Figure 17. This method was compared to the IEA Tar Measurement Protocol, with a reported average tar measurement within ±5% of the results obtained with the IEA tar protocol [53].

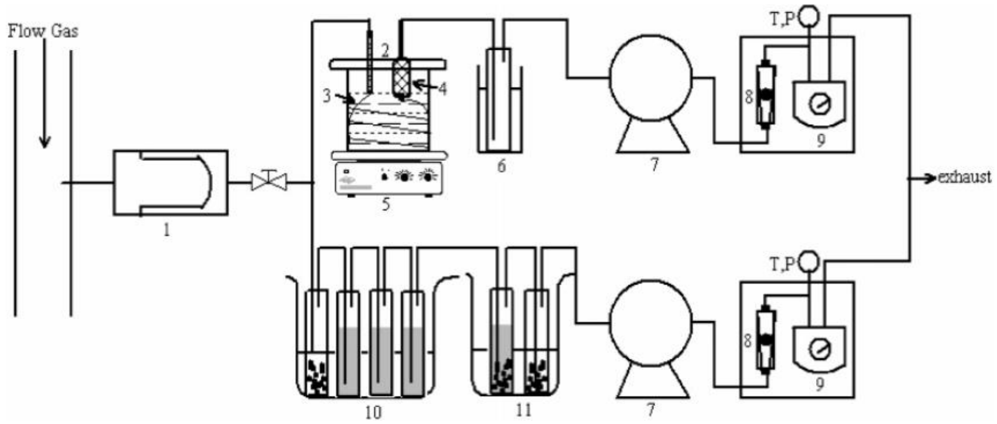


Figure 17. Schematic of the tar sampling and collection system used at Iowa State University. The upper flow path is the dry condenser system, while the lower flow path is the system employed by the IEA tar protocol: (1) particulate thimble filter; (2) pressure cooker; (3) Santoprene tubing; (4) glass-wool-packed canister; (5) hot plate; (6) chilled bottle; (7) vacuum pump; (8) rotameter; (9) dry gas volume meter;(10) water/ice bath; (11) acetone/dry ice bath [53].

2.5.3 Online tar analysis methods

The offline tar analysis methods (mainly tar guideline and SPA, described in Section 2.5.2) offer a major disadvantage, namely the inability of following rapid variations in the gasification process. On top of that, offline techniques are costly, cumbersome and time consuming. The development of techniques for online tar measurement, a hot topic in gas analysis, tries to address the shortcomings of offline methods. Table 7 shows an overview of the developed techniques for the online detection of tars.

Table 7. Overview of methods developed for online tar analysis [2][19][40][54][55][56].

Technique	Partner	Details
FID differential	University of Stuttgart	See Section 0
FTIR	CEA	[56]
GC-FID	VTT, TUD	[19]
GC/MS with electron and laser ionization	TU Berlin	[40]
Ion-molecule reactions-mass spectrometry (IMR-MS)	CEA	See Section 4.5
Laser-induced fluorescence	TUM / TU Berlin	See Section 4.9 See Section 4.3
LED-induced fluorescence	University of Glasgow	[54]
Liquid quench sampling + UV-Vis spectroscopy	PSI	See Section 4.10
Mass spectroscopy	ECN part of TNO	See Section 4.14
Molecular beam mass spectrometry (MBMS)	NREL	See Section 4.8
Photo-ionization detector (PID)	BTG and KTH	See Section 4.7
Tar dew point analyser	ECN part of TNO	[55]
Time-of-flight mass spectrometry (TOF-MS) with laser ionization	University of Rostock	[40]
Total carbon analyser (Inferno)	SFC	See Section 4.4
UV absorption spectroscopy	DTU	See Section 4.11

Given the large number of initiatives in this field in the last years, in this section we offer a brief description of the different developments. The technologies will be described in more detail in dedicated Chapter 4 of this report, and further information about each technique can also be found in the different Factsheets of Document 2.

- The online tar analyser developed at University of Stuttgart monitors the content of hydrocarbons condensable at ambient conditions (tars), by leading the product gas from biomass gasification to a Flame Ionization Detector (FID). Tar contents in the gas between 200 and 20000 mg/m^3 are detectable and the analysis time required is between 60-90 seconds. FID detection is quite sensible to change in flow rate and temperatures; thus, these parameters must be kept constant during the analysis. Comparison of the online analyser with the tar protocol show similar tar concentrations. This analyser is commercially available [57][58]. Factsheet 30 in Document 2 contains further information.

- The Photo-Ionization Detector (PID) continuous online tar measurement technique is the result of the collaborative effort between BTG and KTH. This device uses photons to generate ions which generate a signal. The "proof of principle" measured tars in real gases at two existing pilot gasifiers showed that the PID follows the tar concentration though with values lower than SPA. The PID is very sensitive to flow rate, temperature and pressure and as such these conditions should be kept constant [43][59]. More details can be found in Factsheet 32 in Document 2.

- The work with the fluorescence tar analysis technique carried out at TU Berlin aimed primarily at a compact, robust and easy to use on-line measurement system for continuous tar measurements. The system was named CON-TAR which stands for CONtinuous-TAR-Analyser. The fluorescence light is led into an optical fibre which is connected to a spectrometer. The CON-TAR device was tested at the GoBiGas plant [60] (see Section 3.2.2). Further details about the CON-TAR analyser can be consulted in Factsheet 8 on fluorescence spectroscopy available in Document 2.

- NREL's Molecular-Beam Mass Spectrometer separates the molecules prior to their analysis/detection. Such a device is very valuable if reacting species and in part even intermediates of reaction are to be examined. The system allows versatile research work and it has proven its operability in many research works. However, is has a very high cost and it requires skilled personnel for operation and interpretation of the results [61]. MBMS was used at the Rentech's biofuel plant [62]. More information about the MBMS can be found in Section 4.8 and Factsheet 28 of Document 2.

- PSI applies a combination of liquid quench sampling and UV-Vis spectroscopy for online tar analysis [63][64]. The liquid quench sampling is a step forward with respect to conventional offline tar sampling based on liquid solvents, since it enables the semi-online analysis of the tar-laden solvent solution (compared to the required offline analysis of the solvent in the tar guideline analysis). The liquid quench sampling system is schematically depicted in Figure 18. The gas is drawn by a pump to a quench lance where it is contacted with 2-propanol. The resulting 2-phase flow is compressed to 2 bar, cooled down to approximately -10°C and separated into gas and liquid phases. The gas can be sent to a flow-meter (and optionally to micro-GC analysis), whereas the liquid stream is pumped through a density meter, a UV-Vis cell and a flow meter. The liquid streams can be then sampled into vials for further offline analysis or disposed as waste. The sampling usually takes 20 minutes. The advantage of liquid-phase analysis compared to gas analysis is that the former allows easy calibration (thus, less complex instrumentation is needed) [63]. More details can be found in Factsheet 25 of Document 2.

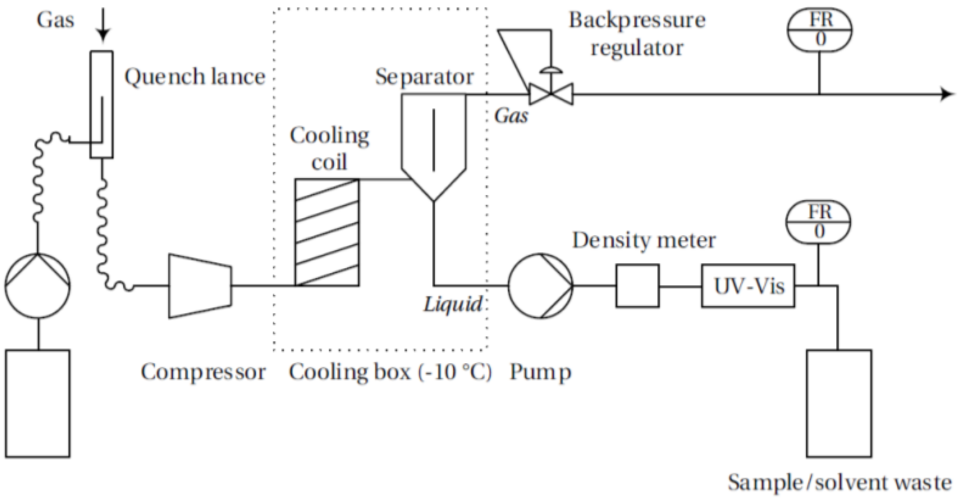


Figure 18. Schematic layout of the quench sampling system (coupled to online UV-Vis spectroscopy analysis) developed by PSI for online tar analysis [63].

- VTT applies a “rapid” online tar analysis based on GC-FID. The chromatographic columns applied are a HP-1 (10 m x 0.53 mm x 0.26 µm) or HP Ultra 2 (25 m x 0.32 mm x 0.52 µm). The analysis time takes approximately 20 minutes, and it can measure online benzene, toluene, naphthalene, phenanthrene, anthracene, fluoranthene, pyrene (and optionally other 20 compounds) [19]. In order to allow the continuous gas sampling, gas dilution is applied (please refer to Section 2.2.4 (b) for more details about the dilution system). Figure 19 shows an example of the results obtained by the application of the rapid tar analysis.

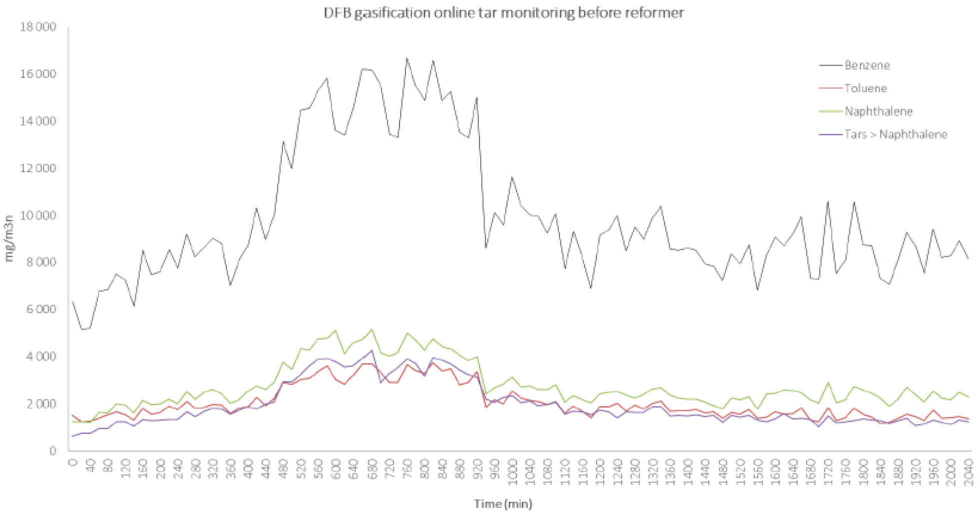


Figure 19. Results of rapid tar measurement applied by VTT [19].

- Technical University of Denmark has developed in-situ, online measurement of tars based on UV absorption spectroscopy. Figure 20 shows the measurement cell for UV absorption (placed inside heated enclosure) used at DTU. In this case, it was concluded that for the application of UV absorption spectroscopy to tar analysis, a temperature range of 250-300°C leads to a trade-off between avoiding of tar condensation and preservation of sharp spectrum profiles [34]. Please refer to Factsheet 44 in Document 2 for more details.

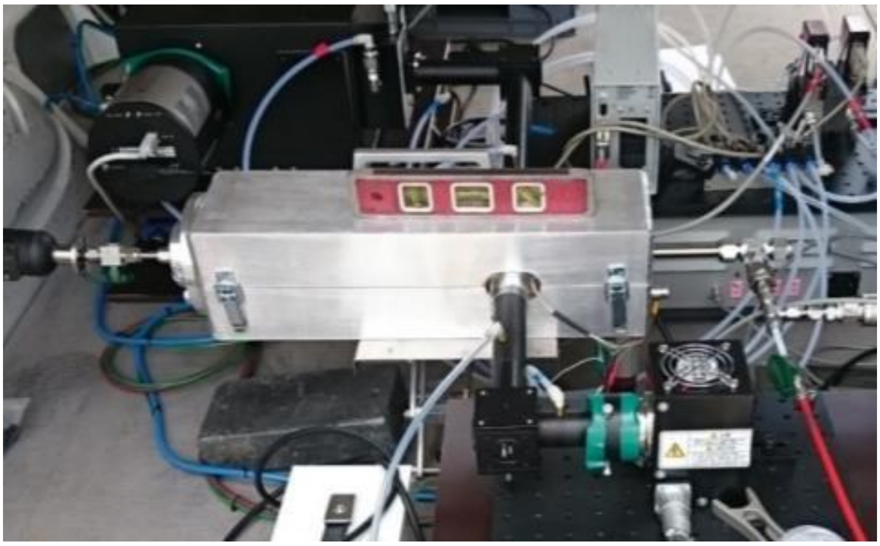


Figure 20. Gas cell for far UV absorption measurements up to 300°C at DTU [65].

2.6 SULPHUR COMPOUNDS

2.6.1 General considerations

During gasification, the sulphur contained in the solid fuel is distributed in the product gas as inorganic and organic species, adsorbed on the char, and in the ash. The fate of sulphur species depends on the feedstock used, the gasification technology and the operating conditions. For both coal and biomass gasification, H_2S has been reported as the main sulphur compound in the gas phase [1][66], followed by COS, CS_2, and thiophene. Sulphur compounds produced during gasification lead to problems of corrosion, catalyst poisoning and pollutant emissions [1][57][66][67]. For example, sulphur leads to irreversible deactivation of Ni catalysts (used in reforming and methanation applications). Therefore, accurate measurement of sulphur compounds down to low detection levels is necessary for the monitoring of gasification-based synthesis processes. Besides the technical problems associated to sulphur, H_2S is a toxic compound, thus its measurement is relevant also for safety issues.

2.6.2 Analysis of sulphur compounds

A good overview on analysis methods for the detection of H_2S in air was already performed in the 1970s by Bethea [68]. The advantages and disadvantages of several techniques -metallic silver plates/filters, lead acetate paper tape, mercuric chloride paper tape, sodium nitroprusside, methylene blue reaction, gas chromatography (GC-FID and GC-FPD), and infrared analysis – were reviewed. Some of the techniques mentioned are not best suited for gasification applications, either because of their very long sampling times, because of the toxicity of the reagents, of because interference issues with other gas compounds. Since then, significant advances have been taken place in the field of sulphur gas analysis.

Micro-GC analysis (GC-TCD detector) is a straightforward option for the online analysis of H_2S and COS. As an example, ECN part of TNO uses a 4-channel micro-GC system with 4 separate injector/columns/detector modules. The column used for the detection of H_2S and COS is a CP740152 PPU (Poraplot) 10 m with backflush. PSI uses a similar system, with the most recent experiences focusing on online measurement of H_2S in biogas rather than syngas [73]. However, the detection limits are relatively high (10 ppmv at ECN part of TNO, approximately 2 ppmv at PSI in biogas applications), thus micro-GC analysis may not be a suitable option if the performance of catalysts and sorbents needs to be properly evaluated (since much lower detection levels are often required). Moreover, the presence of gas analysis pre-sampling systems is not the optimal configuration for the sampling of sulphur compounds. This topic is further discussed in Section 2.6.3.

Table 8. Comparison of some sulphur-selective sensors [71].

	FPD	PFPD	SCD	AED
Ease of use	Easy	Moderate	Difficult	?
Lower detection limit (pg/s)	20	1	0.5	2
Approximate relative cost	€	€€	€€€	€€€€
Dynamic range	10^3	10^3	10^5 (linear)	10^4 (linear)
Equimolar response	Approximate	Yes	Yes	Yes
Other elements detected	P, Sn	P	-	C, H, O, N, Cl (total 26 elements)
Advantages	• Cost effective. • Minimal maintenance.	▪ Long-term calibration stability. • Linear response.	• No hydrocarbon quenching. • Linear, equimolar response to organic S compounds.	• No hydrocarbon quenching. • Linear, equimolar response.
Limitations	• Hydrocarbon quenching. • Non-linear response. • Relatively higher detection limits.	• Hydrocarbon quenching. • The detector must be tuned for specific concentration ranges. • Not compatible with packed columns.	• Complex maintenance. • Reduction of response due to air leakage if proper vacuum is not maintained.	-

GC-FID (Flame Ionization Detector) and GC-MS (Mass Spectrometry) can be used for the measurement of sulphur compounds if they are present at relatively high concentrations. However, if lower concentrations are to be measured (for example, when the efficiency of S catalytic conversion or capture in sorbents needs to be evaluated in synthesis processes), then more selective sensors need to be applied. Among these, the most important ones are FPD (Flame Photometric Detector), PFPD (Pulsed Flame Photometric Detector), SCD (Sulphur Chemiluminescence Detector), or AED (Atomic Emission Detector) [69][70]. The main difference among these selective sensors is the limit of detection, and therefore the price. Table 8 compares these specific detectors used for sulphur measurement. FPD can selectively analyse S-compounds and can also be used for the semi-quantitative detection of unknown S compounds, but at the cost of higher detection limits (10 times higher) with respect to other detectors (PFPD, SCD, AED and GC-MS). Moreover, the calibration and quantification using FPD is difficult due to the non-linear response and the low dynamic range. Compared to conventional FPD, PFPD operates in a pulsed-flame rather than in a continuous-flame mode, thus achieves substantial improvements in both sensitivity and selectivity by lowering the flow rates of the combustible mixtures (i.e., air and H_2) [57][71]. Its linear, equimolar response is another advantage with respect to GC-FPD.

GC-MS is quantitatively more accurate than GC-FPD, with lower detection limits. Moreover, splitless injection can be implemented in combination with GC-MS in order to further decrease the detection limits [71], thus achieving detection limits of ca. 0.5 ng compound/mL solvent (= 5 $\mu g/m^3$ sampled product gas) for most compounds. However, the splitless injection is not suitable for volatile compounds such as thiophene and methylthiophene. GC-MS SIM analysis can detect organic S compounds to about 10 ppb [72].

GC-SCD offers the advantage of having a sulphur-specific detector which is linear over a large range of concentrations. Because its operational principle is based on a chemical transformation of all sulphur atoms contained in analyte samples to sulphur dioxide, an equimolar response to all sulphur compounds is theoretically possible from the detector. The equimolarity of the detector allows the SCD alone (with no preceding chromatography column) to be used a detector for total-sulphur concentrations, which can be useful for detecting low-concentration breakthrough in gas cleaning experiments with sorbents or catalysts (see Figure 24). In gas chromatography, the SCD can also be used in parallel with other detectors. For example, PSI has used a GC-SCD/FID for analysis of sulphur compounds from product gas [64] and biogas [73]. The instrument used includes a single injector followed by two columns (both 40 m DB-Sulfur columns), one for each detector.

Other detecting equipment available for analysis of sulphur-containing compounds includes gas chromatography coupled to Atomic Emission Detector (GC-AED) and gas chromatography coupled to Barrier Ionization Discharge (GC-BID) [70]. The profiles of these analysis techniques can be found in Factsheets 12 and 13 of Document 2, respectively.

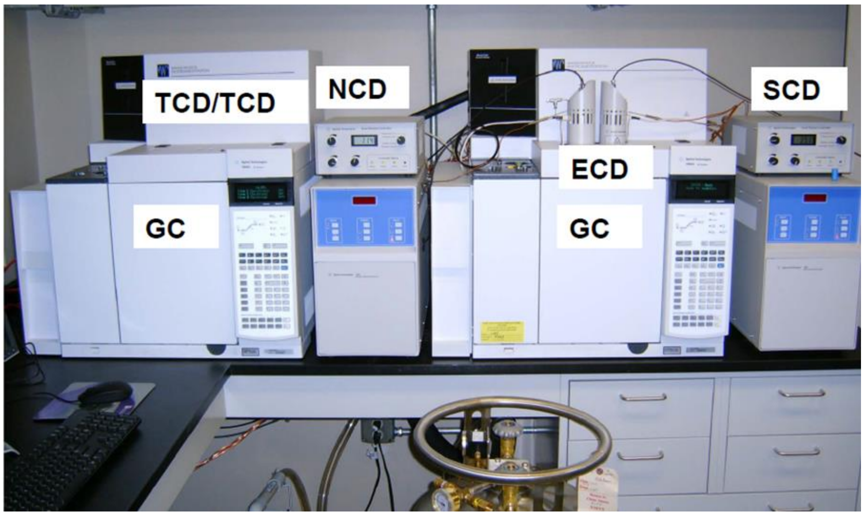


Figure 21. GC equipment applied at Iowa State University for online determination of S- and N compounds (including SCD detector for sulphur compounds, NCD detector for nitrogen compounds, and ECD for nitrous oxide) [76].

Figure 22. GC-FPD (right) and GC-FID equipment for measurement of sulphur compounds and C_1-C_6 hydrocarbons, respectively. Courtesy of ECN part of TNO.

Figure 23. UV fluorescence total sulphur analyser. Picture courtesy of Tübitak Mam [80].

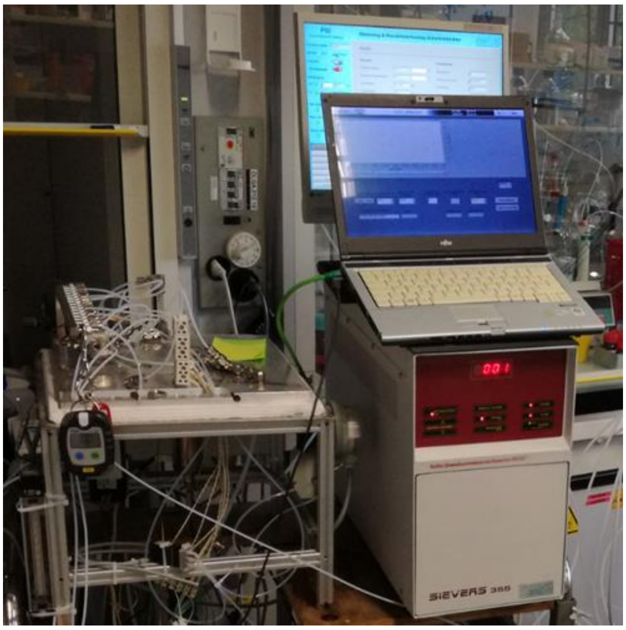


Figure 24. Stand-alone SCD (with no preceding chromatography column) used at PSI for total sulphur measurements. Picture courtesy of PSI.

Table 9. Overview of analysis techniques used for measurement of S compounds at different institutes.

	H_2S/COS	Other S compounds
CEA	Micro-GC Colorimetry OF-CEAS IMR-MS	-
CIEMAT	Micro-GC (GC-TCD), GC-FPD	Micro-GC, GC-FPD
DTU	GC-MS	GC-MS
ECN part of TNO	Micro-GC (GC-TCD) GC-FPD	GC-FPD GC-MS
ENEA	GC-FPD	GC-FPD
ENGIE Lab CRIGEN	Micro-GC Colorimetry OF-CEAS	GC-MS
Iowa State USCD	GC-SCD	GC-SCD
PSI	Micro-GC, stand-alone SCD	GC-SCD
VTT	GC-FPD	GC-FPD GC-BID
TU Delft	GC-PFPD	GC-PFPD
TU Graz	GC-PFPD	GC-PFPD
TUM	Colorimetry	-
TU Delft	Micro-GC, colorimetry	-

Table 9 contains an overview of analysis techniques applied at different centres for the detection of sulphur compounds. Online measurements with micro-GC for analysis of H_2S and COS is applied as an example at CIEMAT and ECN part of TNO. The information collected by micro-GC analysis is often complemented with online, semi-online or offline methods for the measurement of other organic S compounds. For example GC-SCD is used for the analysis of sulphur compounds at University of California at San Diego (gas-sampling valve), at Paul Scherrer Institute (liquid analysis of samples collected by liquid quench), and at Iowa State University [66][74][75]. Figure 21 shows for example the GC system applied at Iowa State University, including an SCD detector for the online measurement of H_2S (up to 1000 ppmv), COS, CS_2, SO_2 and mercaptans, with a detection limit of 10 ppb for these compounds. It is critical that sampling lines and filters are coated with silcosteel®, sulfinert®, or silconert® to prevent sulphur compounds from adhering to surfaces that would produce inaccurate measurements [76]. Many partners use GC-FPD (CIEMAT, ECN part of TNO, ENEA, VTT) or PFPD (TU Delft, TU Graz, Tübitak Mam). GC-BID is applied at VTT for the measurement of S-compounds other than H_2S and COS because of its high sensitivity, which makes it suitable for the detection of trace compounds [77]. However, BID is not applied in a regular basis, but as a complementary tool for GC-FPD [78]. GC-MS is applied by DTU, whereas colorimetry is applied by TUM and TUD for the detection of H_2S [79]. Tübitak Mam also applies UV fluorescence for the measurement of the total sulphur concentration in the gas (Figure 23), with a measurement range of 0-10000 mg S/L, and a detection limit of 5 μg S/L [80]. CEA and ENGIE Lab CRIGEN successfully compared the quantification of H_2S using colorimetry, micro-GC and OF-CEAS (tests with dilute gas; heated gas lines are needed if raw product gas is to be analysed) [81].

2.6.3 Sampling of sulphur compounds

In Section 2.6.2, the available analysis methods for the detection of sulphur compounds have been briefly reviewed. These analysis techniques can be used in online and offline applications. Online detection can be further classified in real-time/continuous and semi-online/intermittent, the latter for example if a gas chromatograph takes a sample every 10-60 minutes. In offline methods, the sampling of the sulphur compounds is performed through a medium and later brought into the detector. Several methods have been applied for the sampling of sulphur compounds from gasification product gas:

Tedlar gas bags:

Gas samples for the sampling of H_2S, COS and other S compounds are collected with Tedlar gas bags, and GC-FPD analysis is afterwards applied. This methodology is applied by VTT, ENEA and ECN part of TNO. In special cases in which a very low detection level (ppb) is required, VTT applies GC-BID or PD-HID as complementary analysis [78]. ECN part of TNO and ENEA collect their sample in a similar fashion but use a GC-FPD instead for the analysis.

Pipettes:

DTU (Technical University of Denmark) collects gas samples with pipettes and injects them directly into a GC-MS.

SPA sampling:

ECN part of TNO has adapted the tar SPA analysis for the measurement of organic S- compounds. For this purpose, standard LC-NH_2 material [32] is used, and the samples are measured with GC-FPD and/or GC-MS. Further details on the SPA methodology can be found in Section 2.5.2 and in Factsheet 37 of Document 2. Details about the implementation of SPA analysis for the measurement of sulphur compounds are specifically discussed in Section 2.6.5. ENGIE Lab CRIGEN have reported the application of SPA (Carbotrap column) for the quantification of thiophene [81].

Wet trapping with impingers (wet chemical analysis):

In wet chemical sampling (please refer to Factsheet 47 of Document 2 for more details), the product gas is bubbled in impinger bottles containing a certain solution where the sulphur is absorbed. Several procedures are applied:

- LNEG applies the EPA Method 11 [82]. Sulphide is retained in an absorbing solution of $CdSO_4$ and then analysed by iodometry.

- University of Stuttgart has adapted a method based on the DIN 51855-4 guideline [83], where gaseous H_2S reacts with zinc acetate forming a solid zinc sulphide precipitate which is subsequently quantified by iodometric titration. For gas sampling, a series of 4 impinger bottles is used. The first impinger is filled with a mixture of isopropanol and sulfuric acid for tar and moisture removal. The second and third bottles are filled with are filled with a zinc acetate solution for H_2S capture, and the last bottle is left empty to collect discharged solution. The accuracy of this method was found to be ±5% [2][3].

- Technical University of Munich measures H_2S with a colorimetric analyser and with a GC-TCD. Colorimetry was also applied by TU Delft for detection of H_2S [79].

- Tübitak Mam analyses tar compounds in isopropanol on a GC-PFPD [69].

- At PSI, offline sulphur measurement is performed using the liquid quench setup (see Factsheet 25 in Document 2). Then, analysis of organic sulphur compounds condensed in liquid solvent samples is performed with GC-SCD (see Factsheet 16 in Document 2).

- ENEA measures the content of H_2S in the product gas by GC-FPD. In order to preserve the system by possible contamination and fouling caused by the presence of tar, before injection in the chromatographic system the product gas is pre-treated for tar removal by gas washing in isopropanol and ultimate cleaning and drying. The sampled gas is then injected in the GC system through a gas valve system and then addressed to a split/splitless injector used to eventually reduce the amount of gas injected into the column if required. H_2S is measured by using a 5-level calibration curve in the range 0.2 – 50 ppmv. Based on the chromatographic method set, each analysis typically lasts 5 minutes. He is used as gas carrier. The detector flame is supported by feeding the torch with a mix H_2/air [84].

- University of Seville applies a train of 4 impingers, each of which is filled with 30 mL of a 5% vol. $CdSO_4$ [85]. Recently, it has been reported that online H_2S analysis is performed using UV spectroscopy [86].

- At VTT, H_2S gas samples are collected from hot wet gas using an electrically heated sampling probe and pumping first 5 minutes to the bypass line and then into Tedlar gas bags. The H_2S determination must be performed within 6 hours from sampling. H_2S and COS are measured with GC-FPD. All gas lines are made of Teflon because H_2S can easily be adsorbed on steel and glass surfaces [20]. Therefore, when starting H_2S measurement, the GC system is pre-treated with H_2S to prevent the sulphur in the sample from adsorbing to the gas lines. For the calibration of the equipment, gas mixtures with different concentrations for H_2S and COS are used. The calibration mixtures are diluted with nitrogen as a carrier gas. With calibration, there must be at least 3 calibration points near the sample concentration, because of the non-linear response of the FPD detector.

A very important aspect to take into account when designing a gas sampling train for sampling of H_2S is that this compound is very reactive, and gets selectively adsorbed on glass and metals surfaces, thus negatively affecting the quantification [20]. As an example, during gasification tests at TU Delft using online GC-PFPD it was found out that the sampling was not reliable, since the gas line to the analyser was too long with stainless steel parts which – in particular with low sulphur loads in the gas - caused loss of sulphur species [71]. Loss of sulphur compounds in sampling lines depends mostly on three factors, namely the type of material, the concentration levels, and the gas flow rates [87]:

- Selection of materials: the use of stainless steel in the analysis lines should be avoided, whenever possible, and inert materials such as Teflon lines, or ceramic (e.g. quartz or SiC filters) should be used instead [20][88]. However, it is claimed that the use of Teflon as tubing material can also result in loss of sulphur compounds (e.g. H_2S) due to its permeability [87]. Sulfinert®-coated stainless steel [89][90] or fluorinated ethylene propylene (FEP) sample bags [91] provide the lowest reactivity and are thus recommended for low concentrations and long residence times [87]. Stainless steel is acceptable for small fittings, since the surface will get passivated after a certain amount of time of constant flow. For high sulphur levels (> 50 ppmv), stainless steel regulators and flow controllers are acceptable as well as aluminium gas cylinders.

- Since surfaces adsorb a given amount of sulphur molecules, losses will relatively smaller if a large flow rate of sulphur molecules are provided. Therefore, the gas flow rate should also be sufficiently high (2-3 NL/min) to reduce adsorption problems [20]. For sulphur levels below 1 ppmv, high flow rates are recommended relative to the surface area inside the lines and fittings that are in contact with the sample.

- The sampling lines should be reconditioned (e.g. back-flushing with nitrogen) when a feed gas with a different composition is sampled [20].

- Adsorption of S in char: particles should be removed at a sufficiently high temperature to avoid sulphur adsorption in the char particles. These outlines can be applied to the sampling of NH_3, HCN and HCl [20].

2.6.4 Organic sulphur compounds

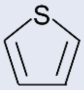
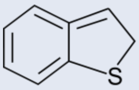
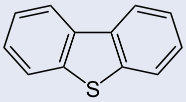
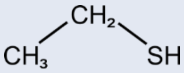
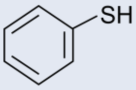
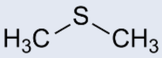
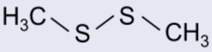
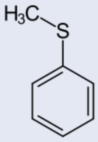
Besides the major H_2S and COS compounds, other organic sulphur compounds such as thiophenes and mercaptans are also produced in coal and biomass gasification [1][66]. Some relevant organic sulphur species that can appear in gasification product gas are listed in Table 10. Despite their low concentrations in general, compounds such as thiophene and its derivatives can lead to deactivation of catalysts, for example nickel catalysts used in reforming and methanation. Consequently, it is important to track the effective conversion or removal of these compounds (in catalytic reactors or sorbents) from the product gas. Therefore, the analysis of the fate of these species in a gasification plant is necessary for the assessment of the performance of the gas upgrading train.

The need for accurate analytical methods for the determination of organic sulphur compounds present in syngas was already identified as early as the 1950s. Wainwright and Lambert [67] adapted the indophenine reaction (deep blue colour formed by the reaction of thiophene with isatin) applied for liquid hydrocarbons to the determination of thiophene contained in syngas from coal gasification. The absorbing solution was composed of 50 mL of concentrated sulfuric acid and 4.5 mL isatin-ferric sulphate solution. The colour intensity of the solution was then measured with a spectrophotometer and correlated with the temperature and the concentration of sulphur in the solution. This method had a detection limit of $1.2 \cdot 10^{-7}$ g thiophene sulphur/mL solution. The ageing of the reagent and the absorption temperature were factors that influenced the test. Moreover, a major drawback of this method was that mercaptans and unsaturated hydrocarbons interfered with the test. The ethylene content of syngas must not exceed 2-3% vol. for reliable results.

Defoort et al. [35] tested an IMR-MS (ion molecule reaction mass spectrometry) as an on-line method for the measurement of tars. Even though thiophene could also be detected, no calibration was available. Thus, only semi-quantitative results based on applying the benzene sensitivity were reported.

Kaufman Rechulski et al. [66] identified the organic sulphur compounds present in product gas from wood- and grass gasification using a combination of a liquid quench sampling system and GC-SCD (sulphur chemiluminscence detector). Using this analysis method, they detected thiophene, methylthiophene, dimethylthiophene and benzothiophene, as well as some other unknown sulphur compounds. The detection limit depended on the amount of steam in the sampled gas, but it could be as low as a few hundreds of ppb, and in the worst case in the 1 ppm range [93]. The sampling conditions, particularly the gas/liquid solvent flow ratio, could affect the capture efficiency of condensable compounds. Even though higher gas/liquid ratios could help increase the concentration of interest compounds in the liquid sample, the condensation of steam contained in the gas also made the solution more diluted. Too high gas/liquid ratios resulted in incomplete capture of condensables into the quenching liquid [66]. Moreover, it was shown that the liquid quench interfered in the measurements of downstream equipment [93].

Table 10. Examples of organic sulphur compounds [70][92].

Group	**Compound**	**Structure**
Thiophene and thiophene derivatives	Thiophene	
	Benzothiophene	
	Dibenzothiophene	
Mercaptans (thiols)	Ethylmercaptan	
	Phenyl mercaptan (thiophenol)	
Sulphides and disulphides	Dimethyl sulphide	
	Dimethyl disulphide	
	Phenyl-methyl sulphide (thioanisole)	

McCaffrey et al. [94] used GC-SCD for the measurement of H_2S, COS, mercaptans, organic sulphides and thiophenes down to ppb level. Molecules that interfere with the measurement are benzene and thiophene (because of coke formation in the SCD reaction tube), H_2S (since it is usually several orders of magnitude higher than other sulphur compounds), and H_2 (since it can deactivate the SCD reaction tube). For this reason a dilution of the sample might be recommended (e.g. via 10:1 split), thus increasing the level of quantification [87][94].

ECN part of TNO uses GC-FPD for the semi-online quantification (analysis of gas bags) of H_2S, COS, thiophene, CS_2, mercaptan, mercaptan derivatives and thiophene derivatives (see Factsheet 15 in Document 2 for more details about the compounds detected). The GC-FPD analyser has 3 ranges of detection: range 0 (0.02 – 8 ppmv), range 1 (0.5 – 25 ppmv), and range 2 (5 – 120 ppmv). During typical wood gasification tests, H_2S is usually above the detection limit even at the highest range of detection (thus, GC-TCD is used instead for the quantification of H_2S).

Sarioglan et al. from Tübitak Mam compared the performance of UV fluorescence and GC-PFPD in samples from a round robin campaign in the framework of the BRISK project [96]. Both analysis techniques gave comparable results (Table 11, results expressed in total amount of sulphur). The analyses revealed the presence of thiophene, benzothiophene and dibenzothiophene. However, the application of SPA did not produce measurable results and was thus discarded. Section 0 discusses in more detail the application of SPA for the measurement of organic sulphur compounds.

Sánchez-Hervás et al. [95] report unsuccessful attempts to apply micro-GC for the measurement of organic S species (research within the current ESCOGAS project), mainly due to limit of detection issues (thiophene) or difficulties to handle heavy species (benzothiophene and dibenzothiophene). For this reason, GC-SCD will be applied instead.

Table 11. Comparison of UV fluorescence and GC-PFPD by Tübitak Mam for the measurement of sulphur compounds (expressed as total S) [96].

	Concentration (mg S/L)	
	UV fluorescence detector	**GC-PFPD**
Gas sample 1: after tar removal	11.45	9.72
Gas sample 2: inlet HDS reactor	11.99	11.47
Gas sample 3: outlet HDS reactor	1.83	0.57

2.6.5 Application of SPA for measurement of organic S compounds

In comparison with H_2S and COS, S- and N- organic compounds (so called S- and N-tars, including volatile compounds and PAHs) can also be sampled using similar or identical methods to those used for tars like the tar guideline or the SPA analysis [44][47][48]. This potential overlapping, which is schematically depicted in Figure 25, can result in synergies between diagnostic techniques. In this sense, there has been an increasing interest to develop a ‘sulphur protocol’ equivalent to the already existing ‘tar protocol’ [97][98]. Research efforts on this direction were initiated during the BRISK project.

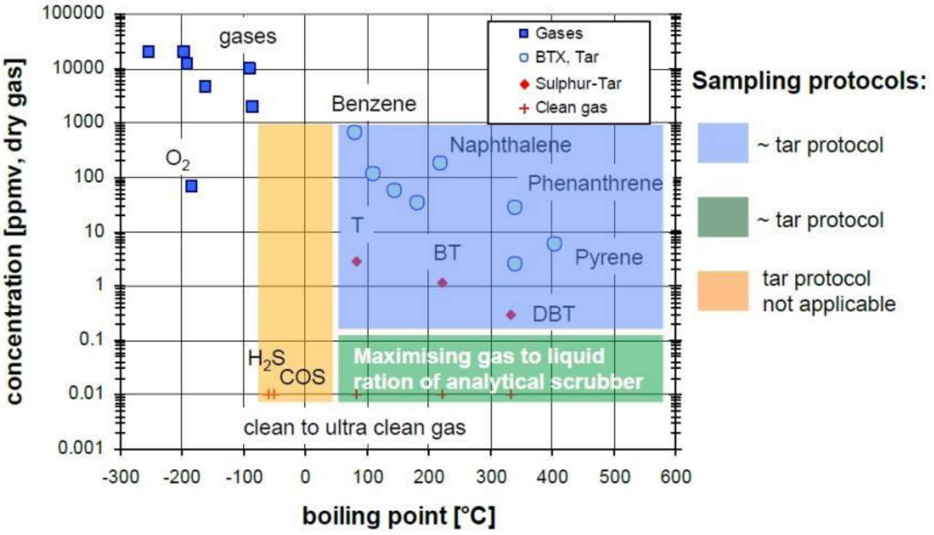


Figure 25. Boundaries of the tar protocol application for the detection of sulphur compounds [69].

ECN part of TNO has worked in the last years in the adaptation of the tar SPA analysis for the measurement of organic S- compounds. For this purpose, standard LC-NH_2 adsorbent columns have been used, and the samples are measured with GC-FPD. SPA analysis for measurement of thiophene was performed for the first time in 2008 using dichloromethane as recovery solvent. A preliminary validation test was performed to determine the extraction recovery efficiency. The recovery results showed that the standard SPA material LC-NH_2 can capture 100% of benzothiophene and heavier organic S compounds, but less than 20% of the more volatile thiophene and methylthiophene, in an equivalent way as benzene and toluene behave in the standard SPA tar analysis (see Section 2.5.2 and Factsheet 37 on SPA in Document 2). Therefore, these light volatile compounds cannot be quantitatively determined with SPA. On the contrary, the heavier sulphur organic compounds could be well recovered from the SPA material.

Further tandem SPA tests using 2 SPA columns (2 amino-phase NH_2 in series) [98] revealed that the first SPA cartridge (standard LC-NH_2) is not reliable for the capture of volatile tar and S compounds, and gets too warm during the sampling of hot product gas under real sampling conditions. Even the addition of a second SPA cartridge could not ensure the complete capture of light S organic compounds. The use of a single SPA cartridge was >95% reliable for benzothiophene and heavier compounds, as well as for polar compounds such as pyridine. Active cooling of the cartridge during the sampling stage might improve the capture of volatile compounds (see Factsheet 37 in Document 2 for relevant outlines and recommendations in SPA sampling).

The addition of active carbon to the standard SPA material (columns in series) was also studied. Although the capture of thiophene was slightly increased, the capture was still poor (concentration only 6% of that measured with gas bags/GC-FPD). Apparently, the capture of thiophene is even more demanding than capturing benzene, even though thiophene has a slightly higher boiling point. Probably, the ratio between concentration and vapor pressure is a more relevant parameter [98]. The poor adsorption of thiophene and methyl thiophene in the SPA material might be due not only to their volatile nature (i.e. to the vaporization from the material), but also to the weak bond formed between the compound and the SPA material. This means that their non-polar nature might play a role in the adsorption behaviour. The adapted SPA method was compared in different tests with gas bags/GC-FPD analysis and the tar guideline method. In all cases the poor agreement between the methods for light sulphur compounds led to the conclusion that quantitative analysis of (methyl)thiophene by SPA sampling is not reliable [71][98].

The application of SPA for the measurement of S aromatic compounds is also being studied by CIEMAT in the ESCOGAS project, where analytical methodologies for monitoring of sulphur species are being developed as support for testing of novel sorbents for warm clean-up of product gas [95].

2.7 NITROGEN COMPOUNDS

2.7.1 General considerations

Nitrogen contained in coal and biomass is mainly converted into NH_3, HCN, HNCO, nitrogen oxides, N_2 and organic nitrogen during gasification [99]. These compounds can poison downstream catalysts, become the precursors to emissions of nitrogen oxides, or pollute wastewater streams, among other problems [1][79][99]. NH_3 and N_2, and to a minor extent HCN, are the main nitrogen compounds produced in gasification of solid fuels [1][79][99][100][101]. Both the structural formula and the content of fuel nitrogen in the biomass feedstock significantly affect the formation and evolution of nitrogen species during biomass gasification [99][101]. Moreover, the introduction of steam in the gasification process has been found to play an important role in converting a large proportion of the fuel-N into NH_3 and HCN by providing H radicals on the char surface [100][102]. As for nitrogen organic species, pyridine has been identified as the major compound present in tar from pressurized fluidized bed gasification of biomass, although the distribution of the compounds depends on the nitrogen content in the fuel [99].

2.7.2 Measurement of NH_3 and HCN

Table 12 shows an overview of the different techniques applied by different partners that have participated in this report. The different approaches applied will be described below in this section.

Table 12. Overview of techniques applied by different partners for measurement of NH_3, HCN and other organic N compounds.

	NH_3, HCN	**Other N compounds**
BE2020+	FTIR Wet chemical analysis	-
CEA	Wet chemical analysis FTIR OF-CEAS	-
CIEMAT	-	GC-MS, HPLC, SPA
DTU	FTIR, UV	Petersen column + GC-MS
ECN part of TNO	Wet chemical analysis	SPA
ENEA	Wet chemical analysis	Wet chemical analysis
Iowa State University	Wet chemical analysis Online with GC-NCD	-

	NH_3, HCN	Other N compounds
TU Delft	FTIR	-
TU Munich	Wet chemical analysis	-
University of Seville	Wet chemical analysis	-
University of Stuttgart	Wet chemical analysis	-

a) Offline measurement of NH_3 and HCN:

The (offline) measurement of ammonia and hydrogen cyanide is usually carried out using wet chemical analysis. This method consists of the sampling of gas through an absorption solution placed in a train of impinger bottles set at 0-5°C. The target compound reacts upon contact with the absorption solution. The resulting loaded solution is then offline analysed. Ammonia being a basic compound, it needs to be sampled in acidic solutions (usually dilute H_2SO_4 or HCl), whereas HCN is captured in basic solutions (often dilute NaOH) [20]. More details about wet chemical analysis can be found in Factsheet 47 in Document 2. Some examples of impinger configurations for wet chemical analysis of N compounds are listed below:

- At VTT, ammonia is collected into impingers containing a dilute aqueous solution (5%) of sulphuric acid. The samples are then analysed with the Kjeldahl titration method according to standard ASTM D1426-03 [103]. The results were compared with online NH_3 measurement using FTIR analysis. As can be seen in Figure 28, there is a relatively large deviation between both analysis methods. For the capture of HCN, a dilute aqueous solution (10%) of sodium hydroxide is used. The HCN sample is then analysed with a static head space-method developed at VTT, using GC-FID.

- At University of Seville, ammonia is sampled using a 5 vol.% H_2SO_4 solution placed in 2 impingers in series (150 mL solution per flask). HCN is sampled in a similar configuration but using a solution of 5 vol.% NaOH [85].

- At ECN part of TNO a slipstream of gas is bubbled for the capture of NH_3 through a trap consisting of 2 impingers in series containing 0.1 M HNO_3 solution in a cooled bath at 4°C. This is the same solution used for the capture of HCl, which can be simultaneously sampled (although HCl can be also separately captured using demineralized water or iso-propanol). The solution is afterwards immediately stored at 4°C in polyethylene bottles. The samples are analysed within 5 days by Ammonia Flow Injection Analysis (AMFIA). The analysis has a measurement range of 0.5 ppmv - 20 vol.%, with an uncertainty of 0.1 ppmv [104]. In the case of HCN, a similar configuration using a 2.5 M NaOH solution is used. The sample is then stabilized to a pH between 10 and 14 (depending on the amount of co-absorbed CO_2) [105], and is then handled according to the NEN-EN-ISO 5667-3:2012 standard [106]. Figure 26 shows as an example the solutions after gas sampling.

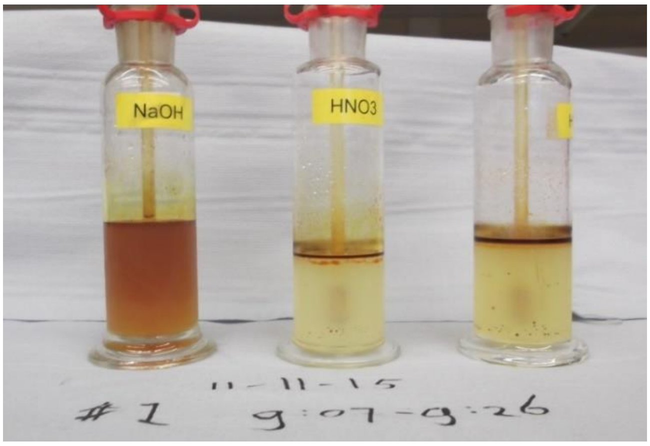


Figure 26. Solutions contained in impingers after gas sampling for offline measurement of NH_3 and HCN. Picture courtesy of ECN part of TNO.

- LNEG uses the EPA CTM-027 method [107]. Ammonia is retained in an acidic absorbing solution of H_2SO_4 and then potentiometrically analysed with a specific ion electrode.

- At University of Stuttgart, gaseous ammonia is absorbed in a 1 M H_2SO_4 absorption solution. The ammonia concentration in the absorption solution is subsequently analysed by photometry according to DIN 38406-5 [108]. For the gas sampling, a series of 4 impinger absorption bottles is used. The first impinger bottle is filled with a mixture of isopropanol and NaOH solution for tar and moisture removal. To avoid NH_3 absorption in the first impinger bottle, the pH value is increased by NaOH addition. The second and third bottles are filled with sulphuric acid for NH_3 capture. The last bottle is left empty to collect discharged solution. The accuracy of this test was determined as ±20% [2][3]. For HCN measurement, the gas is bubbled through a 2.5 M NaOH solution and the solution is then analysed by UV-VIS spectroscopy.

- At ENEA, the sampling procedure for NH_3 is based on wet absorption in a 2-5 wt.% H_2SO_4 quenched aqueous solution. The gas is bubbled through a sampling train system consisting of 3 impingers in series. Each impinger is filled with about 150 mL of the absorption solution placed in brine bath kept at around 0°C. The impingers are connected to each other through PTFE tubes. The system is completed by a fourth impinger filled with silica gel to remove any trace of humidity and preserve the gas pump used to suck the gas stream. In a typical condition the gas is sampled for around 30-40 minutes at a flow rate of about 5 L/min. At the end of sampling the 3 impinger solutions are mixed together into a single sample. Each impinger and the connecting tubes are then washed with fresh absorption solution and all the fractions added to the previous main collected solution. The final solution of sampling is then analysed via spectrophotometry. To quantify the NH_3 in the product gas, amounts of sampling solution are filtered on a 0.45 µm PTFE filter and diluted, and then treated with a commercial kit for spectrometric analysis. The quantification is carried out through a 5-level calibration curve covering a concentration range of 2-190 mg/L. The relevant absorbance signals are acquired at a wavelength with a maximum in the range 660-712 nm by using a double beam, UV-VIS spectrophotometer [84].

- Norton and Brown from Iowa State University [88] measured NH_3 with a gas sampling train formed by 3 impingers in a cold bath at 0°C. A gas flow of 2 NL/min gas was sampled for 15 minutes. The first 2 impingers were filled with 200 mL of a 5 vol.% HCl solution, whereas the last impinger was filled with a desiccant. A specially-designed condenser operating above the water dew point (102°C) was placed upstream the impingers in order to allow tar removal while avoiding water condensation. Although the solution samples were firstly analysed with ion chromatography, the erroneous results resulted in the alternative selection of titrimetric method for the analysis of the samples. An overall measurement uncertainty of ±5% was reported [88]. Broer et al. [22][109] used a similar sampling train to measure HCN with impingers filled with 100 mM sodium hydroxide. HCN was then offline analysed with an Ion Chromatograph (IC).

- Vienna University of Technology [110] applies a set of 6 impingers bottles with the following configuration: the first 3 impingers contains a 0.05 M H_2SO_4 solution (50 mL in the first impinger, 100 mL in the second and third impingers). The fourth and sixth impingers are empty, and the fifth impinger contains 100 mL toluene. The resulting sample is then analysed with ion chromatography.

- Zeisler and Kleinhappl from BE2020+ suggest aqueous 10 mM $Hg(CH_3COO)_2$ at pH 1 as absorbing medium in impinger bottles for the measurement of HCN. Due to the formation of stable $[Hg(CN)_2]_{aq}$ complexes, long-term stability of real samples is ensured. Analysis of HCN is performed by UV-VIS spectrophotometry.

A relevant issue when applying wet chemical analysis (either H_2S, NH_3, HCN or HCl) is to avoid losses of the target compound upstream the impinger train in order to prevent the underestimation of the measurement. Losses can occur either upon tar removal, due to interaction with other product gas compounds (e.g. formation of NH_4Cl), by sorption in the walls of the sampling lines, or by water condensation [88][109]. The sampling train (materials and layout) should be accordingly designed with these considerations in mind. The sampling system must either remove heavy tars without loss of NH_3 or avoid tar condensation [88].

In the specific case of HCN sampling in wet chemical analysis, HCN can be also captured in acidic solutions and polar solvents like acetone if tar removal or NH_3 sampling are performed upstream the absorption with the alkaline solution, thus leading to serious underestimation of the HCN content in the gas, as found by researchers at Iowa State University. Therefore, sampling of NH_3/tar and HCN in series should be avoided and should be rather performed in parallel or in turns [109]. Moreover, during HCN sampling, co-absorption of the CO_2 contained in the product gas can occur ($2\ NaOH + H_2CO_3 \rightleftarrows Na_2CO_3 + 2\ H_2O$). Therefore, it is necessary to apply measures (such as the setting of several impingers in series, or the increase of NaOH concentration in the sampling solution) in order to ensure that all the HCN contained in the gas is effectively captured in the solvent [105]. In order to address this issue, at ECN part of TNO it was calculated the minimum amount of NaOH necessary to be able to potentially absorb all the CO_2 contained in the product gas (upper limit, since an equilibrium takes place in practice) to ensure that sufficient NaOH was available to absorb also HCN. Tests were then performed using a train of 3 impingers in series (2 wash bottles filled with 200 mL of a 2.5 M NaOH solution followed by a guard impinger with 150 mL of the same solution) to assess whether complete capture of HCN could be performed. In order to assess the co-absorption, the CO_2 concentration was online measured during sampling before and after the impinger trains. For the processing of results, it was necessary to apply a correction to account for the reduction in the sampled gas volume caused by the significant capture of CO_2 in the impingers. The results of the experiment showed that, despite the fact that the pH of the solution decreased from 14 to 11-13 as a consequence of the acidification caused by the co-absorption of CO_2, the pH was still high enough to ensure the capture of HCN (even so, CO_2 was not completely captured in the impinger train, as shown by the non-zero CO_2 concentration in the outlet gas). From this test, it was concluded that the HCN contained in the gas could be fully absorbed in the first 2 impingers. Underestimation of HCN can also occur if the gas sampling train is located downstream a gas cooler or other device that removes water from the gas, since a fraction of HCN will end up in the condensate. In this case, it would be recommended to quantify the amount of HCN contained in the condensate, or alternatively, select the gas sampling location upstream the removal of water.

b) Online measurement of NH_3 and HCN:

Fourier-Transform Infrared Spectroscopy (FTIR) can be applied for the online measurement of nitrogen compounds, including NH_3 and HCN in gasification applications. FTIR is applied with this purpose at Bioenergy 2020+, the French Alternative Energies and Atomic Energy Commission (CEA), Finland Research Centre (VTT), Technical University of Denmark (DTU), and Technical University Delft (TUD). Figure 27 shows as an example a typical FTIR spectra of product gas obtained at TU Delft.

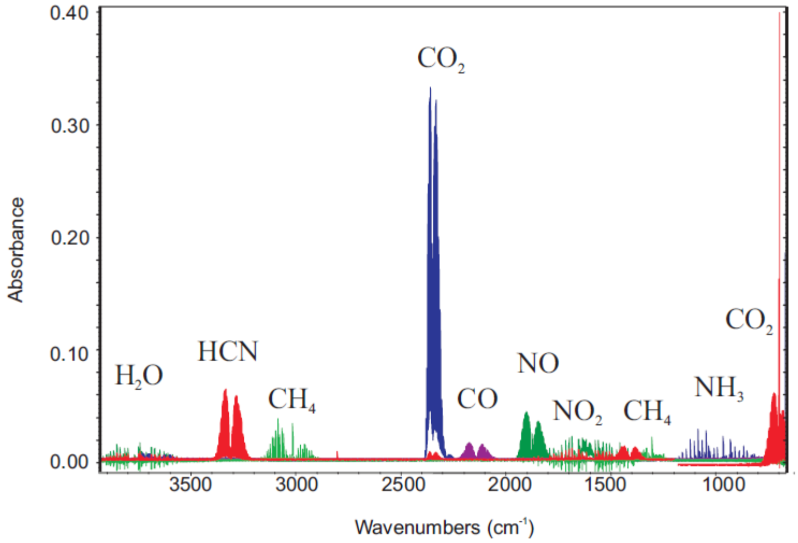


Figure 27. Spectral regions of gases typically present in pyrolysis, gasification and combustion processes [111].

In order to be able to apply FTIR analysis, the product gas needs to be properly conditioned. At VTT the gas is diluted with nitrogen in a dilution system in order to prevent FTIR analysis chamber saturation of the gas matrix (the schematic setup can be seen in Figure 8 and is described in Section 2.2.4). The results of online FTIR were compared with results of offline wet chemical analysis of NH_3 (Figure 28).

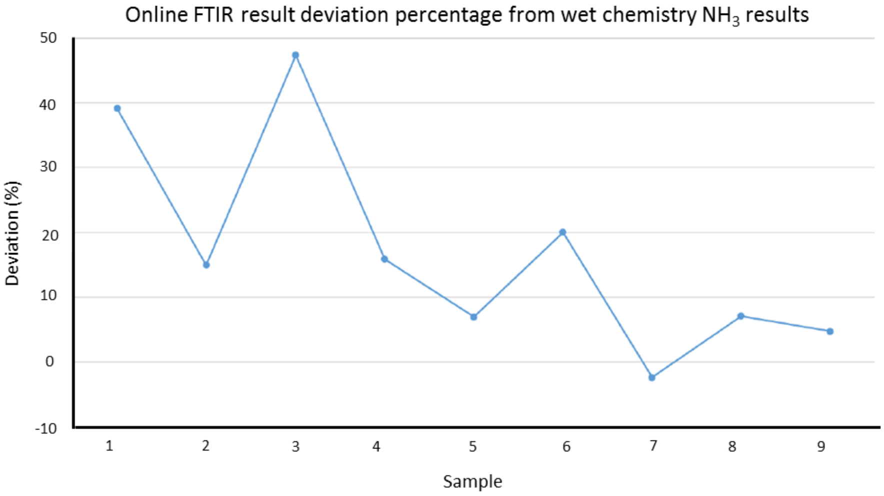


Figure 28. Comparison of results of online measurement of ammonia using FTIR and offline analysis using wet chemical analysis [19].

FTIR and UV absorption are also applied at Technical University of Denmark for the detection of NH_3 (and CH_3Cl). NH_3 is difficult to measure using UV absorption due to its smooth broad spectral structure and strong interference with PAH compounds in the 200-230 nm range, and therefore shorter wavelength measurements (170-200 nm) are needed. On the contrary, NH_3 keeps a unique absorption profile in the IR spectral range [34]. The high-resolution FTIR method was implemented in the LT-CFB and Pyroneer gasifiers (see Section 3.2.6) [34]. Online FTIR is performed with gas extraction at 150°C and in-situ (directly across the gas line at about 530°C). For other N-compounds, such as indoles and quinolones, DTU uses a Petersen column to collect the compounds and then GC-MS for the analysis (please refer to Factsheet 34 in Document 2 for more details about the Petersen column).

Technical University Delft has extensively applied FTIR analysis for the online determination of N compounds in combustion, pyrolysis and gasification applications [21][111]. One of the FTIR units was implemented in its pressurized CFB gasification unit (Section 3.2.13).

Besides spectrometry techniques, gas chromatography coupled to nitrogen chemiluminescence detector (GC-NCD) is applied for online analysis of nitrogen compounds (NH_3 and HCN) from product gas at Iowa State University. GC-NCD can detect nitrogen to ultra-low detection limits (10 ppbv lower detection limit) [76]. The detector is part of a unique GC equipment which has 11 channels and 5 different detectors (see Figure 21). For high levels of NH_3 (> 500 ppmv), GC-TCD can be used [76].

CEA implemented FTIR at the exhaust of the bubbling fluidized bed (LFHT) reactor coupled with the PEGASE high-temperature reactor [112] (see Section 3.2.23). The comparison of results from wet chemical sampling and FTIR for NH_3 measurements revealed the existence of a matrix effect of H_2O on NH_3 quantification. The scientific reason is related to gas/gas interaction when partial pressures are high (> few vol.%). This effect is called collisional broadening. From the results of this study, it appears that H_2O can induce an important error (close to 50%) on the NH_3 quantification by FTIR if it is not considered in the calibration method. A mathematical model has been developed and validated with product gas from biomass gasification experiments. This model is similar to the so-called coefficients of cross-correction encountered in some FTIR gas calibration software. Further details about the effect of collisional broadening and the mathematical model to account for this effect can be found in Factsheet 10 of Document 2. The main gaseous species of syngas such as CO, CO_2, H_2O and NH_3 can be currently online quantified by FTIR with good confidence at CEA.

2.7.3 Organic N compounds

Ammonia (followed by HCN) is the most abundant nitrogen species present in gasification product gas. However, there are also other organic nitrogen compounds present at lower concentrations which can cause deactivation of downstream catalysts. As explained in Section 2.7.2, the capture of ammonia is relatively well known and validated through wet sampling. For the measurement of N-compounds, a number of methods have been reported:

- Aigner et al. [113] used a sampling train similar to that used for the collection of tars (see tar guideline in Section 2.5.2) for the measurement of organic N compounds. The tar solution was afterwards GC-MS analysed. Among the tar compounds measured, some nitrogen-containing species (quinoline, isoquinoline, indole, carbazole) were detected, and combined into a single group of aromatic nitrogen compounds for reporting.

- Mandl et al. [114] measured the nitrogen-containing tars produced in updraft fixed gasification by means of a tar sampling train for the gravimetric quantification of tars. The composition of tars (C,H,N) was subsequently measured using an elemental analyser. It was found that 58-68% of the fuel-N is released in tars, but no further information on the composition of the nitrogen-containing tar is reported.

- Sárossy et al. [115] analysed tar from a 100 kW circulating fluidized bed gasifier operating with straw at 650°C. Tar was sampled using a Petersen column, and the resulting solution was GC-MS analysed. With this method, it was quantified that the gas contained 9.8 mg/m^3 indoles, 7.7 mg/m^3 quinolines and 6.6 mg/m^3 benzyl cyanide. Moreover, GC-MS analysis of the gas phase showed that the gas contained 1.2 ppm thiophene and 0.5 ppmv benzothiophene.

- Yu et al. [99] used solid phase extraction (SPE) for the identification of pyridine, picoline, ethylpyridine, lutidine, and (iso)quinoline.

- ECN part of TNO has adapted the standard SPA analysis used for tar quantification to the analysis of organic sulphur- and nitrogen compounds with GC-MS. More details can be found in Section 2.7.4.

2.7.4 Application of SPA analysis for measurement of organic N compounds

As already discussed in Section 2.6.4, S- and N- organic compounds (S- and N- tars) can be sampled using similar or identical methods to those used for tars [71][97]. Most of these methods are based on the condensation in a liquid or the adsorption in a solid material [39].

ECN part of TNO has worked in the adaptation of the tar SPA analysis for the measurement of organic S- and N- compounds. This adaptation allows the analysis of the different organic compounds from a single extract, with minor additional work with respect to the conventional analysis of tars. Figure 29 shows schematically the procedure followed at ECN part of TNO for the analysis of tars, and sulphur- and nitrogen organic compounds. Additional information on the SPA methodology can be found Factsheet 37 of Document 2. In the case of organic nitrogen compounds, the adapted SPA method can quantify the content of pyridines, methylpyridines and quinoline. Compared to tar analysis (where GC-FID is usually applied), GC-MS analysis is used for the measurement of organic nitrogen compounds.

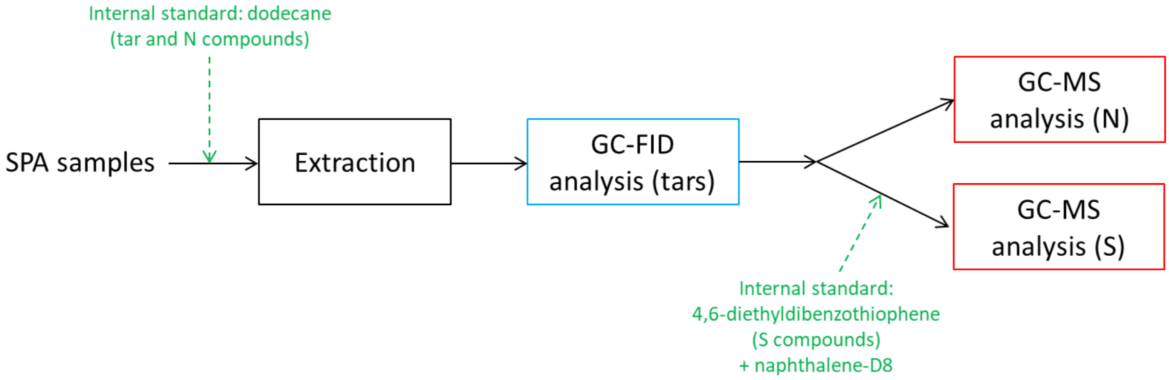


Figure 29. Procedure developed by ECN part of TNO for the extraction and analysis of SPA samples for determination of tars, and S- and N- organic compounds.

The adapted SPA method was compared in several validation tests with results from the guideline method. Unlike light sulphur aromatics (like thiophene and methylthiophene), which cannot be properly captured in the SPA column, the more polar nature of organic nitrogen compounds led to 100% capture for pyridine and heavier compounds [98]. With SPA, compounds like pyridine, (2-, 3- and 4-) methylpyridine, quinoline and iso-quinoline could be measured with a detection limit of 0.1 mg/m^3 (quinoline and iso-quinoline), and 0.25 mg/m^3 (pyridine and methylpyridines). Table 13 and Table 14 show a recent example of the application of the adapted SPA methodology. As can be seen, the product gas from MILENA indirect gasification contains a broad range of organic S- and N compounds. The OLGA tar removal unit can remove the heavier sulphur compounds, as well as the majority of nitrogen sulphur compounds. A large fraction of thiophene is removed from the gas downstream in the BTX scrubbing unit. Finally, the last traces of thiophene and pyridine are captured in an activated carbon bed.

Table 13. Measurement of organic S compounds using SPA at ECN part of TNO fate of sulphur compounds over MILENA gasifier, tar removal unit, BTX scrubbing unit and activated carbon bed. Concentrations in mg/m^3. BT: benzothiophene; DBT: dibenzothiophene [98].

SPA sampling location	Thiophene*	2-Methylthiophene*	3-Methylthiophene*	1-Benzothiophene	2-Methyl-BT	3-Methyl-BT	Dibenzothiophene (DBT)	4-Methyl-DBT	2-Methyl-DBT	46-Dimethyl-DBT	Benzo(b)naphto (21-d)thiophene	Benzo(b)naphto (12-d)thiophene	Benzo(b)naphto (23-d)thiophene
After MILENA gasifier	29.329	10.380	14.499	117.652	16.128	18.559	21.075	3.067	5.620	0.368	3.931	0.782	1.809
After OLGA	25.057	1.628	1.910	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
After BTX scrubber	1.586	<0.05	0.044	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
After activated carbon	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

*: quantitatively not reliable with SPA analysis (see Section 0).

Table 14. Measurement of organic N compounds using SPA at ECN part of TNO: fate of nitrogen compounds over MILENA gasifier, tar removal unit, BTX scrubbing unit and activated carbon bed. Concentrations in mg/m^3 [98].

SPA sampling location	Pyridine	2-Methylpyridine	3-Methylpyridine	4-Methylpyridine	Quinoline	Isoquinoline
After MILENA gasifier	1633.1	339.8	227.8	118.1	558.9	221.0
After OLGA	9.6	1.4	0.3	<0.25	<0.10	0.1
After BTX scrubber	0.3	<0.25	<0.25	<0.25	<0.10	<0.10
After activated carbon	<0.25	<0.25	<0.25	<0.25	<0.10	<0.10

2.8 CHLORINE AND HALOGENATED COMPOUNDS

2.8.1 General considerations

During gasification, the chlorine present in the solid fuel can be released as HCl to the gas phase, whereas a significant fraction remains bound in the ash [116]. The chlorine can also react further with organic species to form chlorobenzenes and dioxins in the gas phase. When the gas is cooled down, the chlorine can condense in the form of alkali salts or as NH_4Cl in the presence of NH_3 [116]. The release of Cl from the biomass fuel has been attributed to an ion exchange between KCl and O-containing groups formed during the devolatilization stage, where Cl is released as HCl [117]. At temperatures above 700°C, the evaporation of KCl was reported to be the primary pathway for the release of chlorine contained in the biomass [117]. Cl is considered as the main facilitator for K release through sublimation of KCl. Approximately 50 wt.% of the Cl contained in corn stover was found to be released below 500°C likely as HCl [118].

Although in general the chlorine content in most biomass fuels is low, certain types of feedstock such as herbaceous biomass, agricultural residues or waste residues can contain significant concentrations of chlorine. Chlorine compounds (HCl, KCl) cause different operational problems in the gasification plant, including agglomeration, deposition, fouling and corrosion, oil degradation and emissions [113].

2.8.2 Measurement of HCl

The measurement of chlorine contained in gasification product gas can be firstly classified in online and offline methods:

a) Offline methods are based on wet chemical analysis (already described in Sections 2.6.3 and 2.7.2). Some examples of application of wet chemical analysis for the determination of HCl are described below:

- ENEA applies a sampling procedure based on wet absorption in a 2-5 wt.% NaOH aqueous solution. The gas bubbles through a sampling train system constituted by 3 impingers in series, each of them filled with ca. 150 mL of the absorption solution. The impingers are placed in brine bath kept at ~ 0°C. The impingers are connected to each other through PTFE tubes. The system is completed by a fourth impinger filled with silica gel to remove any trace of humidity and preserve the gas pump. Typically, the gas stream is sampled for ~30-40 minutes at a flow rate of about 5 L/min. At the end of sampling the solutions contained in the 3 impingers are mixed together in a single sample. Each impinger and the connecting tubes are then washed with fresh absorption solution and all the fractions added to the previous main collected solution. The final solution resulting from the sampling is then analysed via HPIC (high pressure ion chromatography). For this, after proper filtration on 0.45 µm PTFE filter and dilution, the solution is analysed at an ion chromatographic system operating in suppressed conductivity mode. For this analysis a 2.3 mM carbonate/ 0.6 mM bicarbonate solution is used as eluent. The quantification is achieved via a 4-level calibration curve typically covering a 0.5- 10.0 mg/L Cl^- concentration range [84].

- University of Stuttgart applies a series of 3 impinger bottles for gas sampling. The first two impinger bottles are filled with demineralized water. The last bottle is empty to collect discharged solution. Due to the good solubility of Cl containing compounds, the use of an additional tar and moisture removal bottle is not possible. Therefore, the majority of tars and other organic components were removed from the sample solution after sampling and before analysis using a filter for organics. The chlorine concentration in the absorption solution was analysed by coulometry. In coulometry, Cl is not detected directly, but the total dissolved Cl content in the solvent is measured. Besides chlorine, also other electrochemically reactive compounds like bromine, iodine, oxalate, thiosulphate or thiocyanate compounds are detected. Consequently, the Cl measurement results slightly overestimate the actual Cl concentrations in the sampled gas [2][3]. The accuracy of this method was determined as

-20% below the actual concentration of the gas.

- The measurement of HCl in gasification gas is reported by University of Stuttgart to be challenging, since HCl reacts with NH_3 forming ammonia chloride when the temperature drops below 300°C ($HCl (s) + NH_3 (g) \rightarrow NH_4Cl (s)$). The ammonia chloride is dissolved together with other Cl containing compounds in the impinger bottles where the totality of all Cl compounds is analysed. This has an effect on the NH_3 measurement too, but since the Cl content in the product gas is rather low in comparison to the NH_3 content, the relative effect on the NH_3 content is rather low [2][3].

- At VTT, the sample gas flow is led through a washable quartz pipe to the main washing stage (impingers train). The basic assumption is that chlorine compounds in the product gas are water soluble, and therefore the impingers contain distilled water. After sampling, the whole system is washed with distilled water and all water washings are combined to one sample. This gathered sample then analysed by means of capillary ion analysis. The HCl samples are analysed with in an ion analyser, using Ion Select High Mobility Anion Electrolyte with indirect UV at 254 nm detection and silicate capillary 60 cm (length) x 75 µm (internal diameter). Gas chromatography with electron capture detector (ECD) is used for the analysis. ECD is a selective detector for monitoring compounds with high electron affinity such as halogenated compounds. Halogenated compounds can be analysed from liquid or gaseous samples. With gaseous samples, the sample injection is performed with gas valve system that separates 1mL volume sample from the sample stream [78].

- Wet chemical analysis is also applied at ECN part of TNO. In this case, the product gas is sampled through a 3% H_2O_2 solution placed in 2 impingers at 4°C. Alternatively, HCl can also be sampled using demineralized water, iso-propanol, or even simultaneously to ammonia sampling in an acidic HNO_3 solution. Afterwards the solution is analysed with ion chromatography (lower detection limit 1 ppmv). With this method, a HCl content in the range of 2-50000 mg/m^3 can be determined with an uncertainty of 0.2 mg/m^3 [104]. In an earlier work by van Paasen et al., a similar setup but using a 0.05 HNO_3 solution is reported. In this work, it was found out that the interaction between chlorine and dust (caused by the different operating temperature of the dust filter) affected the measurement of HCl in the gas [116].

- University of Seville applies a train of 4 impingers, each of them filled with 30 mL of distilled water. The impingers are placed in a bath filled with ice and water. The gas is finally dried in a silica gel flask to guard the gas pump [85]. The solution is afterwards analysed via ion-selective electrode (ISE).

b) Online methods:

- CIEMAT applies FTIR (see Factsheet 10 in Document 2).

- NREL applies high-resolution magnetic sector mass spectrometry (see Section 4.2).

- A joint research consortium formed by German partners (KIT, Technical University Darmstadt and PTB) have developed an online measurement method based on tunable diode laser absorption spectrometry (TDLAS) for calibration-free, in situ HCl detection [16]. The implementation of TDLAS for HCl detection is described in more detail in Section 2.8.4.

2.8.3 Measurement of other Cl compounds

The term 'dioxins' generically refers to a family of chlorinated derivatives of aromatic ethers, a number of which are very toxic [116]. Under certain gasification conditions gasification (T < 850°C), the formation of dioxins can be possible, all the more if plastic-containing waste feedstock is used in the gasifier.

Van Paasen et al. from ECN [116] performed a complete speciation of chlorine compounds during

RDF and sewage sludge gasification. HCl was measured using the impinger train described in Section 2.7.2, whereas Cl-containing tar compounds were measured using the tar guideline setup (simultaneously to the determination of conventional tar compounds). Micro-coulometric titration in an EOX analyser [119] was further applied to the bulk tar solution. It was claimed that part of the HCl contained in the gas is also dissolved in the solvent used in the tar guideline sampling, thus the measurement being overlapped with the results of HCl from the wet chemical analysis [116].

Wang et al. from Technical University of Denmark [120] report the application of GC-MS analysis for the measurement of methyl chloride (CH_3Cl) contained in product gas. For this, a 100 µL gas sample is taken out from a gas bag or a gas pipette and injected manually into the GC–MS system. The measurement uncertainty was found to be within 5%. DTU has also recently used far-UV spectroscopy for in-situ methyl chloride measurements on the LT-CFB gasifier. The results obtained showed that measured CH_3Cl concentration (120 ppm) at 283°C is approximately similar to that obtained with GC-MS analysis [121][122].

2.8.4 Application of diode laser-based spectroscopy (TDLAS) for online HCl detection

Ortwein et al. [16] report the development of a method based on tunable diode laser absorption spectroscopy for the online, non-intrusive measurement of HCl in a gasification process. Laser absorption spectroscopy, particularly TDLAS, was selected due to its good selectivity and sensitivity, and its high time resolution.

HCl exhibits 3 absorption bands detected by TDLAS: the rotational-vibrational fundamental band (1ν-band, around 3200-4200 nm wavelength), the first overtone band (2ν-band, 1700-1950 nm), and the second overtone band (3ν-band, 1200-1300 nm). The HCl line strengths in the 3ν-band are 1000 times smaller than those at 3500 nm, which implies that either large absorption path lengths or very high optical resolution (thus, considerable effort) is needed. In comparison, the 2ν-band at 1700 nm offers larger line strengths, thus better detection sensitivity. The use of vertical-cavity surface-emitting lasers (VCSEL) opens up the way to the use of the 2ν-band, and therefore, a better trade-off between the required absorption path length and the achievable sensitivity [16].

A challenge of online detection of HCl using laser spectroscopy is related to the strong spectral interference from H_2O and CO_2. To overcome this challenge, it is necessary to identify and isolate a spectral region with minimum interference in order to achieve high sensitivity. The selection of suitable absorption lines is an important parameter in TDLAS analysis, since it influences the accuracy and quality of the measurements. Due to the fact that there is a large number of possible absorption lines, particularly for the interfering H_2O and CO_2, a line selection software was developed to resolve the absorption spectrum for the expected experimental boundary conditions (pressure, temperature, and path length). The application of this software proved that the 2ν-band was suitable for the measurement of HCl. Based on this finding, a vertical-cavity surface-emitting laser (VCSEL) of 1.74 μm was selected.

Another important aspect to consider when applying TDLAS is that a precise measurement requires a good knowledge of the optical, spectral and electronic characteristics of the used laser [16]. The coefficients that describe the variation of the frequency with temperature (dν/dT), variation of frequency with current (dν/dI), and dynamic tuning characteristics of the laser need to be determined.

The developed TDLAS unit was tested at the REGA entrained-flow gasifier (KIT). The schematic layout of the setup, as well as a diagram of the implementation of the optical device in the gasifier, are plotted in Figure 30. The temperature of the laser was kept constant at around 30°C by using a Peltier element. The optical access at both sides of the gasifier consisted of sapphire windows. Nitrogen was used as purge gas in the access pipes to avoid contamination of the sapphire windows. The laser beam was detected by an InGaAs photodiode. The current signal was then amplified, digitized and processed.

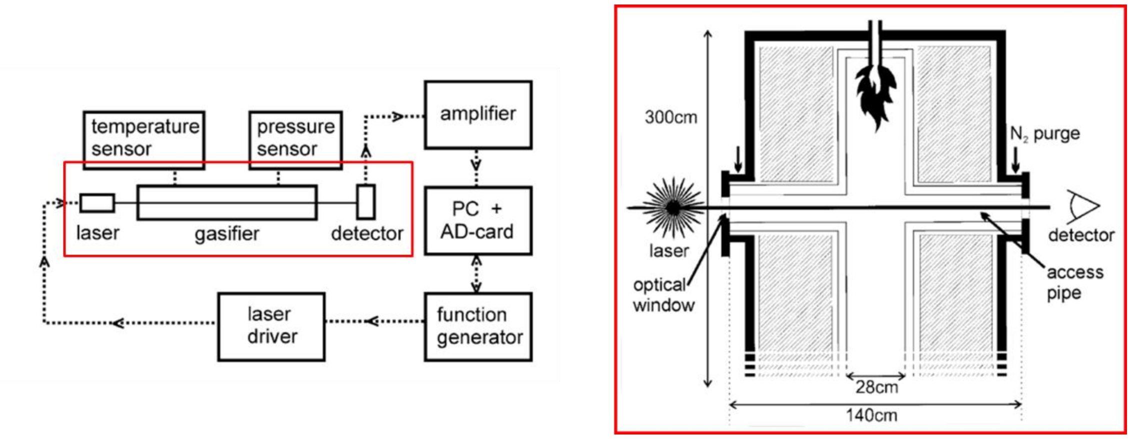


Figure 30. Schematic implementation of TDLAS setup for online measurement of HCl at an entrained-flow gasifier [16].

Figure 31 displays results of the online measurement of HCl during combustion and gasification tests at the REGA gasifier. As can be seen, the TLDAS detector can properly respond to variations in the process conditions, thus showing good time resolution and sensitivity. However, it is noteworthy that significant Cl concentrations were measured, given the fact that ethylene glycol (Cl-free material) was used as fuel (except for a final addition of NaCl to the glycol at minutes 40-45). Even before the operation started, 200 ppmv HCl were measured, which was attributed to the electrical heating of the reactor. A detection limit of 45 ppm (13 ppm ·m) was reported [16]. Further information about the application of TDLAS can be found in Factsheet 43 in Document 2.

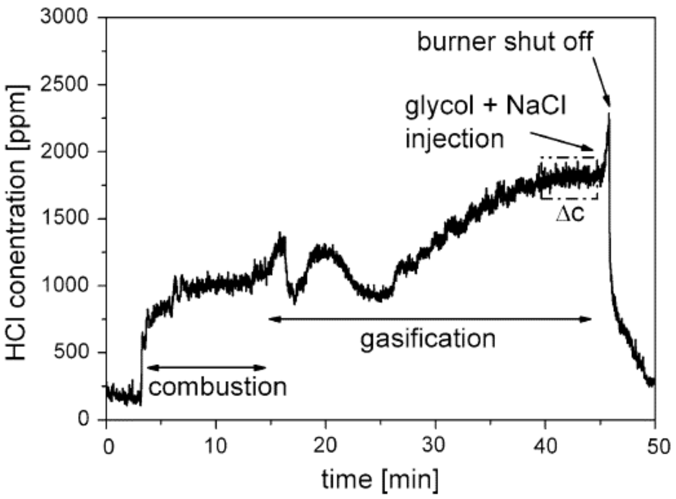


Figure 31. Online measurement of HCl using TDLAS during combustion and gasification [16].

2.9 ALKALI COMPOUNDS

2.9.1 General considerations

The ash chemical composition of the feedstock plays an important role in the operation of a gasifier, since it influences the selection of the gasification technology, of the operating conditions (gasification temperature, type of bed material/additives, etc.), and the selection of the gas cleaning train. Alkali compounds are particularly important since they are involved in reactions leading to deposition, fouling, corrosion, agglomeration and emissions. It is relatively frequent to deal with fuels (either biomass or waste) whose (K_2O + Na_2O)/SiO_2 ratio is near the eutectic point where a minimum in the melting temperature occurs. Alkali compounds such as KCl and KOH are easily released into the gas phase at high temperatures relevant for gasification. The rest of the inorganic and organic potassium remains in the char, where during the char conversion silicates, sulphates, and carbonates are formed. The release of alkali metals in the product gas is influenced by a number of parameters, including the form of the alkalis in the biomass fuel, the gasification pressure and temperature, the heating rate or the equivalence ratio [123]. These vaporised compounds can condense at 500-850°C [116] and deposit on heat transfer surfaces and downstream equipment, resulting in the formation of deposits and slag, and causing blockages, abrasion of pipes and equipment parts (e.g. turbine blades), loss of efficiency in heat exchangers, and eventually unplanned plant shutdown. Several mechanisms for the formation of alkali-derived deposits have been reported, including condensation of inorganic vapours (resulting from the pyrolysis and gasification of the solid biomass), inertial impact, thermophoresis and electrophoresis, and chemical reaction. Related to this, Na and K, together with Cl and S, play an important role in corrosion mechanisms. Despite all these operational problems, alkaline and alkaline-earth compounds have also broadly been identified as catalysts in pyrolysis, combustion and gasification processes [124].

A specific example of the importance of the control of alkali content in the product gas is the application of the gas in gas turbines. Alkali metal impurities react with the sulphur compounds in the combustion chamber of the gas turbine (SO_2, SO_3) to form sodium and potassium sulphates which condense on the surfaces of the turbine and hot gas path. Corrosion can be initiated at 700-900°C when the molten alkali sulphates condense on the metal of the turbine blades, resulting in an attack to the protective oxide of the turbine. Therefore, in order to control deposition and hot corrosion problems, the content of alkali metals in the product gas/syngas has to be minimized.

Table 15. Overview of alkali measurement methods (adapted from [125]).

	Method	**Offline/offline/ in situ**	**Analysis**
	Particles sampling from cyclone/filters/bed material)	Offline	EDS, XRD, XRF, ICP-OES, etc.
Optical	Excimer Laser-Induced Fragmentation Fluorescence (ELIF)	In situ	-
Optical	Tunable Diode Laser Absorption spectroscopy (TDLAS)	In situ	-
Optical	Inductively-Coupled Plasma Optical Emission spectroscopy (ICP-OES)	Gas extraction (online)	
Thermal	Volatility Tandem Mobility Analyzer (VTDMA)	Gas extraction (online)	

With this background, the importance of the measurement of alkali compounds in the gas in order to properly control the gasification process and to ensure adequate removal of alkalis in the gas cleaning train is clear. Alkali measurement methods (see an overview in Table 15) can be firstly classified in offline (analysis applied to the deposited alkalis on the dust particles collected from cyclones and/or filters), and online (applied directly to product gas). The latter allows overcoming the limited time resolution of the former. In general, the considerations on alkali measurement in product gas are closely related to the discussion about measurement of particles (see Section 2.12 of this document).

Although a number of the above techniques have been taken from aerosol science and have been applied in combustion applications, the specific conditions (high temperature, high particle concentration, complex gas mixture including condensable tars) makes measurement during gasification a challenging task, which results in disturbances and unstable measurement [125]. In this report the online measurement method developed by Gothenburg University in Section 2.9.2.

2.9.2 Online measurement of alkali compounds based on SID and VTDMA

Researchers from Gothenburg University [125][126][127] have developed a technique for online measurement of alkali metals based on surface ionization. The principle behind is the controlled nucleation and condensation of alkali compounds and heavy tars to force them into the particle phase, where they can be further analysed using aerosol analysis techniques [125]. The practical implementation of this concept consisted of the quick and continuous extraction and quenching of the gas sample by dilution and cooling to produce sub-micron aerosol particles. The alkali concentration from the aerosol particles was determined by Surface Ionization (SID). Additionally, the thermal stability of the particles was evaluated using Volatility Tandem Differential Mobility Analyser (VTDMA) [127].

When the sample gas enters the probe, it gradually cools down from 750°C to 350°C. During the cooling, alkali compounds condense to particles, whereas most tars still remain in the gas phase. Then, a 2.5 μm cut-off cyclone was applied to remove the larger particles in order to avoid clogging of the system. After the cyclone, the sampled gas is diluted and further cooled with nitrogen in 2 steps. As part of the development of the measurement method, the effect of the dilution setup and the implementation of a thermodenuder (activated carbon bed at 300°C) for prior removal of tars was evaluated [127]. The particles formed in this extraction process are then directed to the different analysers (SID for the measurement of alkali concentration, and VTDMA for the determination of the thermal stability of the aerosol particles). Complementary, the concentration of CO at the outlet of the measurement train was online measured for the calculation of the dilution factor [127].

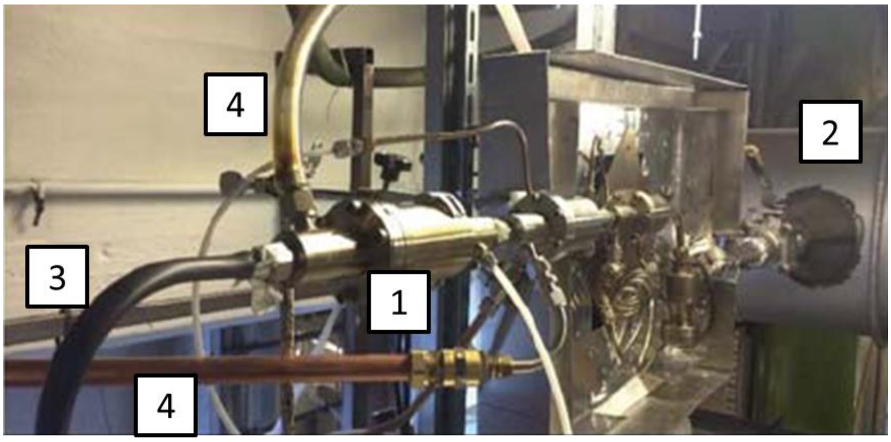
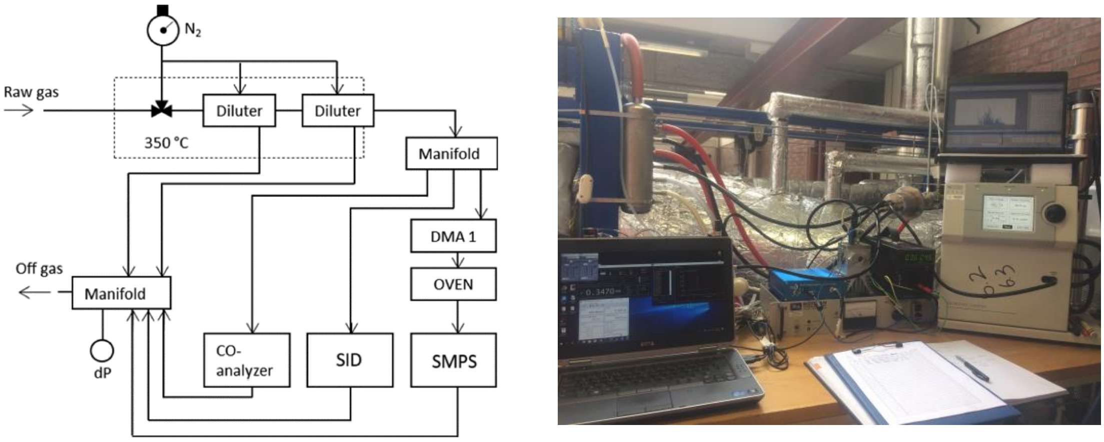


Figure 32. Sampling probe for cooling and dilution of product gas applied by Gothenburg University for online measurement of alkali compounds and heavy tars [125]: 1: Ejector diluters; 2: Raw gas line; 3. Diluted sample gas; 4: Off-gases.

The developed measurement method was applied at pilot scale (the 2-4 MW_{th} dual fluidized bed gasifier at Chalmers University of Technology) [127] as well as in the commercial GoBiGas plant (more than 60 hours of real-time measurement) [126]. Figure 33 displays the schematic layout of the setup implemented at GoBiGas for the online measurement of alkalis during plant operation. The aerosol particles formed during the rapid cooling and dilution of the sampled gas were directed to the surface ionization detector (SID) for measurement of total alkali concentration, and to the VTDMA train (composed of a first DMA, an intermediate oven and a final SMPS) for the measurement of the thermal stability (thus, of the chemical composition) of the particles. Complementary, the SMPS allowed the determination of the particle size distribution. Lastly, the dilution factor was determined via the monitoring of the outlet CO concentration (which was compared to the inlet concentration). The total analysis time for every particle size distribution scan was 2 minutes, whereas the alkali concentration and dilution factor were determined with a time resolution of 1 second [126]. An example of the results obtained with this setup is displayed in Figure 34.



(a) (b)

Figure 33. (a) Schematic layout of the setup for the online measurement of alkali metals in product gas applied by Gothenburg University at the GoBiGas plant [126]; (b) implementation of the SID, picture courtesy of Gothenburg University.

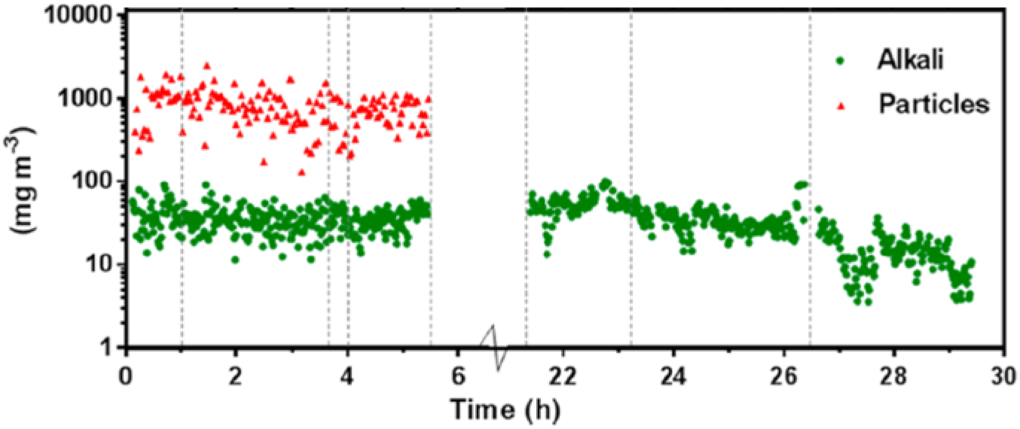


Figure 34. Mass concentration of alkali metals and particles measured at the GoBiGas plant using the online measurement method developed by Gothenburg University [126].

2.9.3 Online measurement of potassium using TDLAS

Tunable Diode Laser Absorption Spectroscopy (TDLAS) is a promising technique for the online, non-intrusive, calibration-free measurement of a number of compounds. Although it has been applied in other applications such as internal combustion engines, power plants, or incineration plants, TDLAS has also been used in gasification processes (mainly in high-temperature gasification of coal or biomass) for the measurement of a number of compounds (CO, H_2O, CO_2, CH_4, temperature, soot content) [14][15][16][17][128].

Sepman et al. [15] from Umeå University have recently reported the application of TDLAS for the measurement of (among others) potassium in gas phase present in syngas. The TDLAS setup was tested in a 100 kW_{th} entrained-flow gasifier using peat and wood as feedstock. The TDLAS setup (Figure 35) consisted on 3 sensor systems placed at ports located at different heights and cross sections of the gasifier:

- Sensor 1 (direct TDLAS system, 2298 nm) was used for the measurement of CO, H_2O and soot fraction. The single scan detection limits for CO and H_2O were 1000 ppmv and 3000 ppmv, respectively. The uncertainties at the core of the reactor were 15% for CO and 20% for H_2O.

- Sensor 2 was applied for the simultaneous measurement of temperature and H_2O using calibration-free scanned wavelength-modulated spectroscopy (CF-WMS) at 1398 nm, and potassium in gas phase at 770 nm using direct TDLAS. The detection limit for H_2O was 1000 ppmv. The setup for the measurement of K(g) had a dynamic range of 40 pptv·cm to 40 ppmv·cm.

- Sensor 3 was used to measure soot by laser extinction (LE) at 639 nm.

The optical access port windows were flushed with N_2 (2 L/min) to avoid fouling and to prevent gasification gas from entering into the extensions. The N_2 flow was selected after evaluating its effect on the measured species.

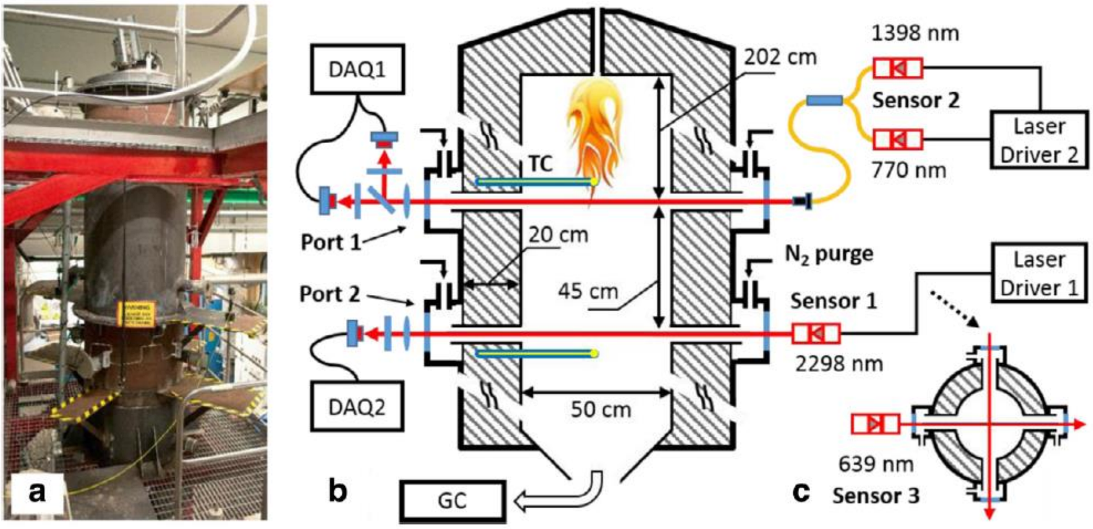


Figure 35. Implementation of TDLAS by Umeå University for online measurement of K, CO, and H_2O in syngas: (a) 100 kW_{th} entrained-flow gasifier at Piteå, Sweden; (b) schematic layout of the implementation of the sensors in the gasifier [15].

The transitions of the sensors were selected so as to have either small or linear dependence of the line strength with temperature. For example, in sensor 1, in the expected range of gasifier operating temperatures, the variation of the line strength with temperature is less than 10%, thus CO concentration can be calculated directly from the integrated measured absorbance. The line strength of the H_2O transition (at 2299 nm) varies 15% within the range of operating temperatures, thus the column density obtained from the spectra can be converted to concentration values by using the T measurement from sensor 2 [15].

Figure 36 displays results of concentration of gas-phase K measured with TDLAS during 2 days (peat used as gasification feedstock on test day 1, and wood gasification in day 2). Based on the measured results, it was estimated that only 0.1-1% of the K present in the biomass was released as K (g) during gasification. The measurements were compared with concentration values calculated from thermodynamic simulations. As can be seen, there is a large discrepancy between the experimental and the equilibrium measurements. It was suggested that the H_2O-derived density-weighted path-averaged temperature might not be the actual average temperature for potassium, and thus the actual absorption path length for K might be smaller than the reference path length (equal to the inner diameter of the gasifier) [15]. There was no further reference for a comparison of TDLAS with results from other measurement techniques for the validation of TDLAS.

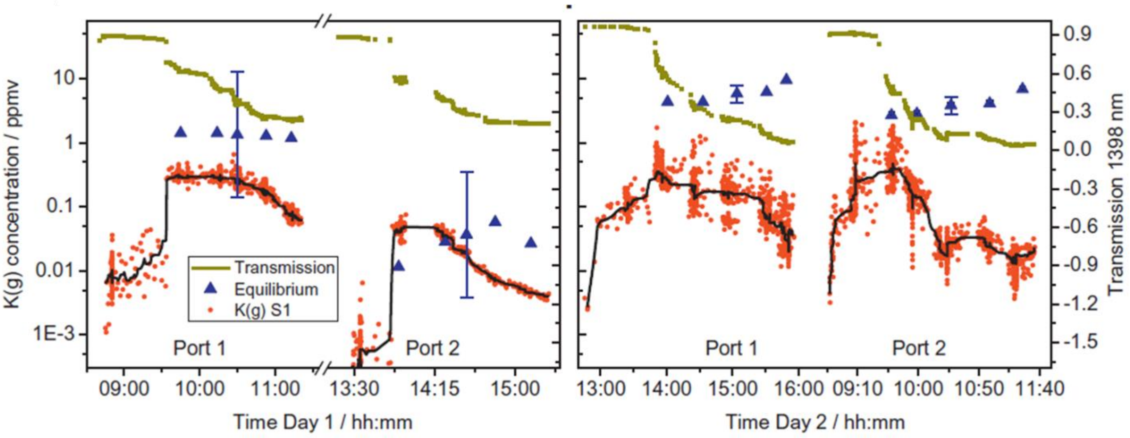


Figure 36. Results of online K measurement using TDLAS: peat (left) and wood (right) as gasification feedstock. Comparison with equilibrium calculations is displayed [15].

2.9.4 Online measurement of potassium using ELIF

Excimer laser-induced fragmentation fluorescence (ELIF) is a laser-based technique that has been applied by Technical University Munich for the online measurement of alkali metals contained in product gas [125][129]. UV light is used to photo-fragment alkali chloride and hydroxide molecules.

2.10 TRACE ELEMENTS

2.10.1 General considerations

Trace elements (Cr, Co, Ni, Cu, Zn, Pb, Hg, As, Se, Sb, and Cd) are relevant compounds in thermochemical conversion processes due to their toxicity and environmental hazard. Although in general the content of heavy metals in most biomass fuels is very low, emissions of heavy metals are an issue in e.g. coal and waste processing plants. For this reason, the measurement of heavy metals (both in gas phase and in solid phase such as fly ash, bed material or filter ash) is a topic of interest in gasification plants due to emission limits. Currently, the mercury emissions are limited at 50 $\mu g/m^3$ [130][131][132].

In the specific case of mercury, the content in biomass and waste fuels broadly ranges between 0.001 mg/kg (meat and bone meal), 0.004 mg/kg (olive residue), 0.01 mg/kg (demolition wood), 0.08 mg/kg (waste paper) and 0.5-10 mg/kg (sewage sludge and RDF) [132]. There are no many data about the fate of mercury in gasification processes, which is claimed to be very different from combustion due to the reducing atmosphere. Existing experimental data indicate that mercury exists mainly in its elemental form in gasification processes [132].

2.10.2 Measurement of trace compounds

The sampling of trace elements present in product gas is mainly performed by wet chemical analysis. Just as explained in Sections 2.7 and 2.8, this method involves firstly the sampling of gas via an impinger train. As an example, at ECN part of TNO a 1 N K_2CrO_4 solution is used in the impingers. Afterwards, the loaded solution is subjected to ICP-OES analysis. Table 16 shows the measurement range and uncertainty of some trace compounds when analysed by ICP-OES.

Table 16. Measurement range and uncertainty of trace compounds measured by ICP (liquid matrix) [104].

Compound	Measurement range (mg/kg)	Measurement uncertainty
Ba, Sr, Mg	0.005 – 20	5%
Cr, Co, Ni, V, Fe	0.01 – 100	5%
Cu, Mn, Ti, Li, Cd, Zn, Al	0.01 - 50	5%
B, Ca, Sb	0.05 - 500	5%
Se, As, Sn, S, P, W, Na	0.1 - 1000	5%
Si, Pb, K	0.5 - 1000	5%

Molecular Beam Mass Spectrometry (MBMS) has also been used by Jülich Forschungszentrum for the online (qualitative) measurement of inorganic compounds in product gas. Zn was one of the species detected by the MBMS unit [133].

2.10.3 Measurement of mercury

There are several offline methods for the speciation of Hg from flue gas (EPA 29, EPA 101, OH method, Tris-Buffer). In general, all the sampling trains consist of a nozzle and isokinetic probe for gas extraction, a filter for removal of particles, and an impinger train filled with liquid solution to capture gas-phase Hg. After sampling, the filter and sorption media are prepared and analysed for Hg in a laboratory. In order to measure oxidized Hg and elemental Hg forms, multiple solutions/reagents are used. Among these methods, the OH (first set of impingers with KCl solution, second set with HNO_3/H_2O_2 solution, and third set with $H_2SO_4/KMnO_4$ solution; further analysis with cold vapour atomic absorption spectroscopy) is the most accepted [132][134]. As for online measurement techniques, there are commercial Continuous Emission Monitors (CEMs) available for the monitoring of mercury in combustion plants [132][135][136]. These equipment units measure only the total gas-phase mercury by reducing the oxidized forms of Hg into elemental form with wet chemical reagents or with catalysts or thermal reduction units. The latter, called dry conversion methods, overcome the challenges of interference encountered by wet reagents (the reducing ability of reagents such as $SnCl_2$ can be affected by high levels of SO_2)[132].

Detection systems include Cold Vapor Atomic Absorption Spectroscopy (CVAAS), Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS), in-situ Ultraviolet Differential Optical Absorption Spectroscopy (UVDOAS) and Atomic Emission Spectroscopy (AES) [132]. The majority of Hg CEM systems uses CVAAS or CVAFS as the detection technique [132]. However, these techniques are susceptible to flue gas constituents like SO_2, NOx, HCl and Cl_2, which can act as measurement interfering compounds [132]. Below a concentration of 5 µg/m^3 of mercury, the AAS systems exhibit lower signals to noise ratios. At these concentrations, the AFS based systems are a better choice. An alternative to Hg measurement approach is AES. In this detector, Hg is ionized by a high energy source (plasma) and the emission energy is measured. The advantage is that all forms of mercury, including particulate-bound Hg, are capable of being ionized and detected. Although this technology is not quite developed, another major advantage is that the ionization source and detector can be located directly at the source, avoiding sample delivery issues. In addition, AES is not susceptible to spectral interferences from common flue gas constituents [132].

As an example, Wendt et al. [131], in a study of mercury sorption applied to coal IGCC applications, implemented a system for online analysis of mercury in the gas phase (Figure 37). For the gas treatment before analysis, 2 wet chemical impinger sets were set in parallel: the first set contained 2 impingers in series filled with a $SnCl_2$/HCl and NaOH solutions, respectively. This impinger train was set for the measurement of the total amount of mercury in the gas (since the $SnCl_2$ solution reduces the Hg species to its elemental form). The second set was composed of 2 impingers in series filled with KCl/$Na_2S_2O_3$ and NaOH solutions, respectively. This set was applied to measure only elemental Hg (Hg^0), the role of the KCl/$Na_2S_2O_3$ solution being removing the oxidized Hg absorption. Therefore, the difference between the measurements of both trains represents the oxidized mercury concentration (speciation by difference). The mercury concentration in the gas phase was then monitored by a cold vapour atomic fluorescence (CVAF) analyser.

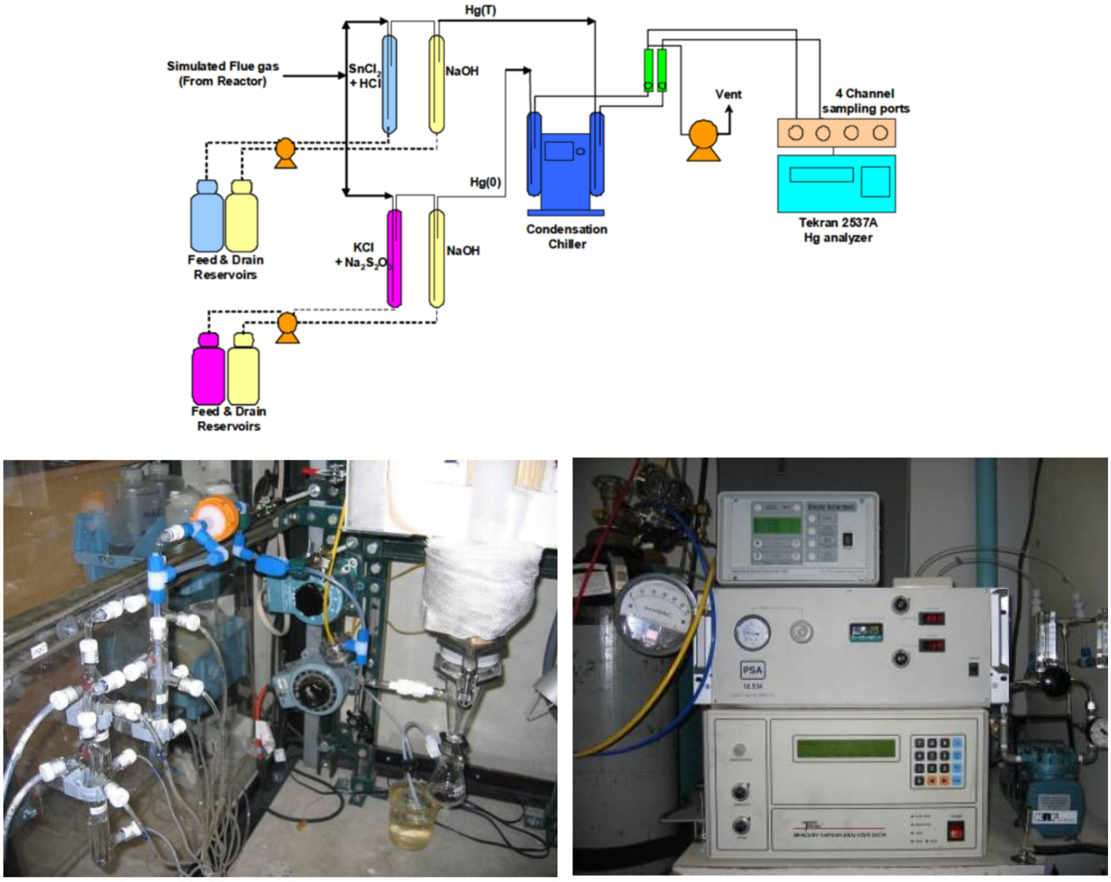


Figure 37. Online measurement of mercury in gas phase by Wendt et al.: schematic layout of sampling and analysis train (top); sampling system (bottom left); cold vapour atomic fluorescence (CVAF) mercury analyser and Hg source calibration system (bottom right) [131].

Gas-phase mercury from gasification can be offline measured at ECN part of TNO using cold vapour AAS (Atomic Absorption Spectrometry) applied to liquid samples from wet chemical sampling. In this case, the measurement range is 0.001 – 0.01 mg/kg, with an uncertainty of 5-10% [104]. More information about AAS can be found in Factsheet 3 of Document 2.

2.11 SILICA COMPOUNDS – SILOXANES

2.11.1 General considerations

Siloxanes are silica-containing volatile organic compounds that come up as a gas-phase impurity mainly in landfill gas and biogas produced from digestion processes, although they can be also present in gasification product gas [137]. The most common siloxane present in biogas is decamethylcyclopentasiloxane (D5). If raw biogas is combusted e.g. in a gas engine or a boiler, siloxanes can be converted to microcrystalline silica sand particles which form deposits (with the appearance of a fine glassy layer [137]) and can eventually lead to system failure [138]. SiO_2 from siloxanes deposits can also be formed on heat exchanger surfaces (which results in decreased heat transfer efficiency), in catalysts and electrodes of fuel cells (which results in deactivation and degradation, respectively). Therefore, the measurement of these compounds is important for the design and efficiency performance of gas cleaning trains in biogas and gasification plants.

2.11.2 Measurement of siloxanes in biogas

The vast majority of literature devoted to measurement of siloxanes is focused in biogas applications, therefore this section briefly covers the analysis of siloxanes for biogas applications. As a general remark, the sampling of siloxanes is very challenging due to their relative high molecular weight and low vapour pressure (i.e. low volatility). At the moment, no standard methods for siloxane sampling have been developed, and most of the currently available measurement methods are offline. Several types of equipment have been reported in literature for the sampling of siloxanes from biogas, namely thermal desorption tubes, impingers, Tedlar bags and canisters (Figure 38). Eichler et al. [138], in a systematic comparison of these sampling techniques for the sampling of D5 siloxane, concluded that thermal desorption tubes and gas sampling with impingers are suitable methods for siloxane sampling. On the contrary, indirect sampling with gas bags or canisters results in incomplete recovery of the siloxanes due to the adsorption to the surface of the gas bags of the gas containers (Figure 39). Additionally, gas leakage from gas containers can also be an issue. It has been reported that 2-3 samples are required for reliable analysis [137].

Figure 38. Available methods for sampling of siloxanes from biogas [138].

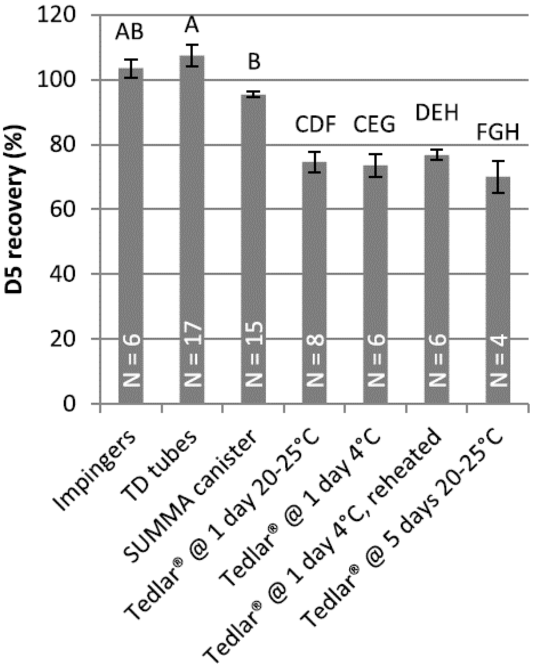


Figure 39. Efficiency of siloxane (D5) recovery using different sampling techniques [138].

The analysis of the sampled siloxanes is usually performed using GC-MS or GC-FID equipment. However, it has been reported that GC columns can degrade in the presence of chlorinated hydrocarbons giving false siloxane readings [137]. Recently, an analysis method based on FTIR spectroscopy has been developed for the online measurement of siloxanes from biogas [137]. This system can analyse the presence of low level (<0.2 mg/m^3) total Si from siloxanes and uses a total siloxane number instead of speciation of the siloxane compounds. The testing of this FTIR-based method was performed at several landfill sites. However, the validation was very difficult due to the inconsistency of the laboratory results with which the FTIR results should be compared. The discrepancies among laboratory results occurred even amongst duplicate samples. The uncertainty and inconsistency factors identified included sample collection, shipping and handling issues, and siloxane conversion during the shipping process. On top of that, the lack of gas standards for accurate siloxane calibrations adds up to the analysis challenges [137].

2.12 PARTICULATE MATTER

2.12.1 General considerations

The raw product gas from gasification contains a certain number of entrained particles. This particulate matter might cause deposits, erosion and corrosion, particularly when dealing with high-ash biomass feedstock [139]. The particles contained in product gas include both carbonaceous matter (char, soot and tars) and inorganic matter (ash from the fuel, nucleated and condensed particles from gaseous compounds, and bed material particles in case of fluidized bed processes) [139]. For the proper design and optimization of specific gas cleaning equipment, it is necessary to measure the properties (concentration, particle size distribution, and number of particles) of the particulate matter contained in the gas.

2.12.2 Measurement of particulate matter

An overview of the available techniques (both offline, as well as online and in-situ) for the measurement of particulate matter contained in gas after sampling is shown in Figure 40. Table 17 compares the capabilities of laser diffraction, SEM microscopy and electrostatic particle counter for the concentration and particle size of particulate matter.

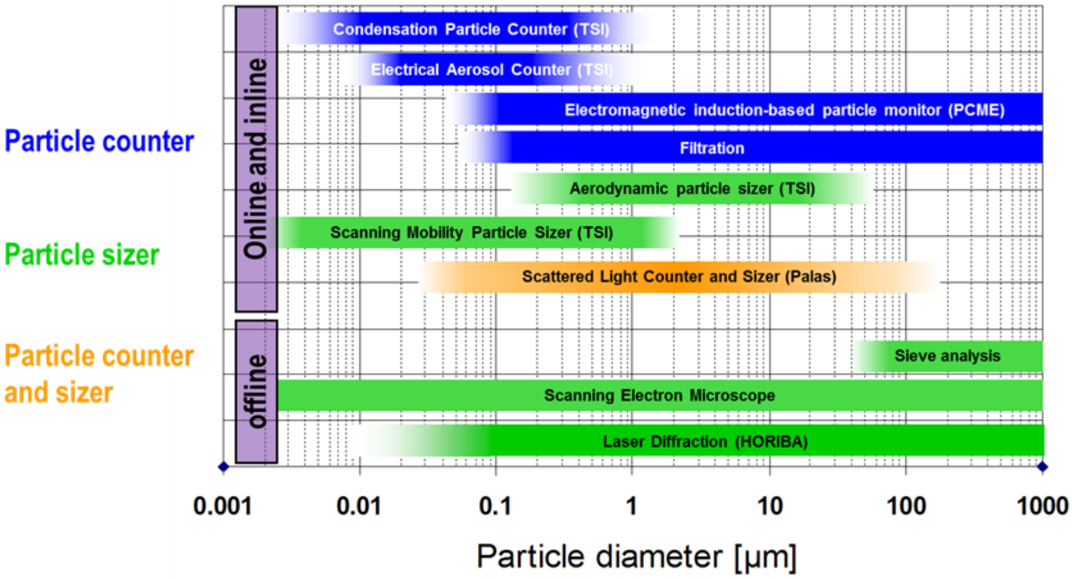


Figure 40. Overview of available methods for measurement and analysis of particulate matter [140].

Generically, the offline measurement of particles contained in gas from thermochemical processing (either flue gas from combustion or product gas from gasification) consists of the separation and collection of the particulate matter entrained in gas while taking a representative sample of the gas. A representative sample means that the concentration, size distribution and composition of the particulate matter in the gas sample remain the same as in the duct gas stream that is being measured. Representative sampling is achieved by operating a sampling probe under isokinetic sampling conditions [69][141]. This means that the velocity of the gas in the probe must be similar to the velocity of the gas stream. This requires a verification of the combination of the right nozzle and pump rate prior to sampling [142]. Since downstream the probe there might be further particle losses due to impaction, sedimentation, diffusion, electrostatic attraction, and thermophoresis, the sampling system should thus be short and straight without changes in gas velocity in order to minimize particle losses [141].

The measurement of dust in product gas from gasification poses a number of specific challenges: on the one hand, the gas is sampled at high temperatures. This implies that the particles in the sample are subjected to physical and chemical transformations [141], but from the practical point of view it also poses higher requirements on materials and equipment [69]. On the other hand, the presence of tars in the gas leads to the risk of condensation on the surface of the particles during sampling at temperatures below 400°C, whereas alkali chloride vapours can condense at temperatures above 500°C [141]. Tar condensation leads to blockage of the nozzles of the measurement equipment, which affects the accuracy of the quantitative determination of the dust content.

Another specific challenge of the offline measurement of particles from product gas is related to the presence of inorganic and organic vapours, which may be transformed into particulate matter during cooling via homogeneous nucleation and condensation [139][141]. If the particle number concentration is high (>10^6 particles/cm^3), coagulation may also take place, thus affecting the particle number concentration and size distribution [141]. In order to prevent these processes, a dilution/quenching probe can be implemented. In a dilution probe, the product gas is diluted with nitrogen at high temperatures to quench particle dynamics (such as particle coagulation, nucleation, and condensation) [139][141][143]. The aim of the dilution probe is to favour the condensation of the inorganic vapours on the probe walls over particulate formation, and to prevent particle coagulation by reducing the particle number concentration [141]. The dilution ratio can be varied by adjusting the nitrogen flow.

Table 17. Overview of features of available techniques for analysis of concentration/particle size of particulate matter [140].

	Laser diffraction	**SEM microscopy**	**Electromagnetic induction-based monitoring**
Sampling mode	Offline	Offline	In situ
Measurement of concentration	No	No	Yes
Measurement of particle size	Yes	Yes	No
Concentration range (mg/m^3)	-	-	0.1 - >1000
Particle size range (µm)	0.01 - 5000	0.001 - 1000	0.1 - 1000
Temperature (°C)	Offline	Offline	Up to 400
Pressure (bar)	Offline	Offline	Up to 50
Principle	Angular variation of light as a laser beam passes through the sample.	Image of a sample by scanning the surface with a focused beam of electrons.	The current induced by charged particles interacting with the sensor rod is proportional to the concentration.
Advantages	Wide range of particle size. Interesting for samples taken e.g. in a filter.	Interesting for samples taken e.g. in a filter. Particle shape can be studied. Very high resolution (down to 1 nm): particles in nanoscale can be detected.	Very flexible in size and concentration ranges. No need for isokinetic sampling.
Limitations	Particles < 10 µm require knowledge of optical properties (refractive index). Particles in	Need for image processing software or manual analysis to determine size distribution.	Need for calibration with secondary method. Required gas velocity when variable gas flow: 8 – 20 m/s. Lower gas velocities

	Laser diffraction	SEM microscopy	Electromagnetic induction-based monitoring
	nanoscale cannot be detected.		are possible if the flow is constant. Condensates interfere with the sensor signal. Proper isolation of the probe from sources of noise and proper grounding is required to limit the electrical noise. The flow field around the sensor is essential: Stokes numbers > 1 are necessary for the sensor rod not to interfere in the particle trajectories.

The most widely techniques for particulate measurement applied to hot gas (either flue gas or product gas) are listed below [69]:

- Filters. An example of the application of filters for particulate matter measurement is in the tar guideline protocol (CEN/TS 15439), described in more detail in Section 2.5.2 of this document and in Factsheet 41 of Document 2. In this case, a heated quartz thimble filter is used. (Offline) gravimetric determination of total particulate matter content is then possible. Soxhlet filters are also broadly used for the measurement of particulates in product gas. A known amount of product gas is sampled through the filter. The measurement range using both types of filters is 10 – 200000 mg/m^3, with an uncertainty of 2 mg/m^3 [104].

- Low-pressure cascade impactors can (offline) determine particle size distribution in the range of 0.3 – 30 μm. This equipment has the advantages of being robust, relatively cheap, and straightforward to operate. Moreover, the sampled particulate matter can be handled for further analysis, e.g. SEM-EDX microscopy, ICP-OES, and elemental analysis [69]. This apparatus is described in Section 2.12.3.

- Dilution probe combined with a Scanning Mobility Particle sizer (SMPS). This equipment consists of a differential mobility analyser (DMA) and a condensation particle counter (CPC). Particles are differentiated (range of 10-700 nm) based on their mobility in an externally applied electric field. This equipment is described in Section 2.12.4

- Dilution probe combined with an Aerodynamic Particle Sampler (APS). This is an online, laser-based method, which can determine the particle number size distribution based on the aerodynamic particle dimension in the range of 0.5 – 7.5 μm.

Table 18 presents an overview of the capabilities of different institutes in measurement of particulate matter from product gas.

Table 18. Overview of methods for measurement particulate matter in product gas.

Institution	Equipment used	Applications
Abo Akademi University	Low-pressure impactor	Combustion and gasification processes
BE2020+/ TU Graz	High-temperature impactor (HTI)	Combustion and gasification processes
ECN part of TNO	Cascade impactor SMPS	Combustion and gasification processes
Linnaeus University	APS SMPS ELPI LPI TEOM	Combustion and gasification processes
PSI	Electromagnetic induction-based particle monitor (PCME) SMPS Laser diffraction SEM	Gasification, methanation
TU Delft	Cascade impactor	Combustion and gasification with high steam content in gas
VTT	Electrical low pressure impactor (ELPI)	Gasification
Gothenburg University	SMPS	Gasification and combustion

An example of a probe used for the sampling of particulate matter in gas (flue gas or product gas), with a cascade impactor mounted on top of it, is shown in Figure 41. It is a steel probe equipped with an internal temperature control system. During ash sampling, the hot ash-laden gas is quenched by nitrogen. To prevent condensation in the sampling tube, the temperature of the flue gas sample is kept above the condensation temperature at all times. To prevent clogging, the mouth of the sampling probe can be rotated away from the flue gas stream when no samples are taken.

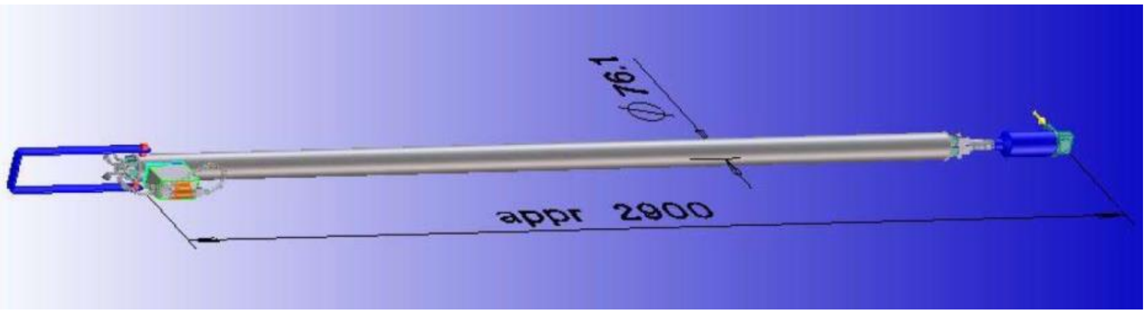


Figure 41. Schematic of the dust sampling probe configured for in-duct cascade impactor measurement used at ECN part of TNO [142]. Dimensions in mm.

2.12.3 Low-pressure cascade impactors (LPI)

A cascade impactor performs an aerodynamic classification of particle sizes of dust contained in a gas stream. Figure 42 shows a schematic of a cascade impactor. It is composed of a number of orifice plates (called jet stages) of different cut sizes (cut diameter, d_{50}) through which the gas flows. Each jet stage contains nozzles which differ in their number and diameter. When the particles pass through the nozzles of each stage, the direction of the gas flow is changed (Figure 44), and the particles are deposited based on their inertia on a certain collection plate or they will flow to the next impactor stage. The size of the collected particles decreases along the impactor until the last jet stage where fines are collected.

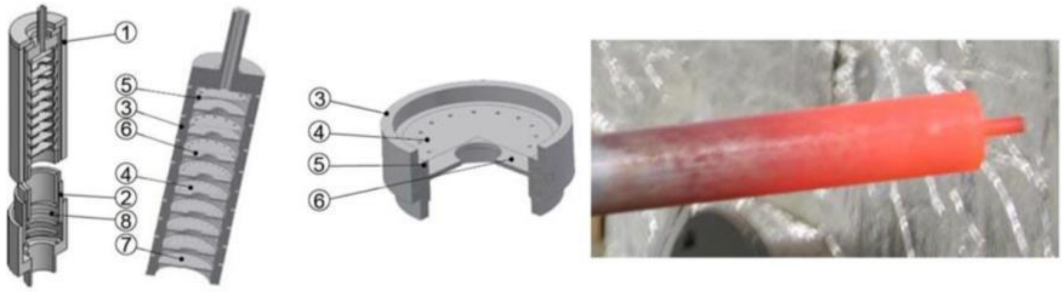


Figure 42. Schematic of high-temperature cascade impactor (left); high-temperature cascade impactor from BE2020+ after operation (right) [69]. Legend: 1. Outer casing; 2. Inner casing; 3. Shell; 4. Orifice plate; 5. Spacer ring; 6. Stagnation plate; 7. Critical orifice; 8. Spring.

Figure 43 shows the Pilat Mark V cascade impactor (used for example by ECN part of TNO and TUD), whereas the configuration of the jet stages of this impactor is summarized in Table 19. The pre-cutter and the right-angle attachment allow sampling at high dust conditions and/or perpendicularly to the gas stream. These devices also contain a deposition plate, where coarse ash (>50 µm) is deposited. Although both devices have exactly the same function, they differ significantly in geometry. The right angle attachment is more compact, thus allowing for a better temperature control, yet its aerodynamic diameter is significantly larger than that of the pre-cutter. The pre-cutter has less impact on the flue gas flow around the impactor inlet, and it is thus better suited for sampling in small ducts and at high flue gas flow velocities [142].

Table 19. Configuration of the cascade impactor used at ECN part of TNO for measurement of particle size distribution of particulate matter contained in product gas.

Stage name/number	Type	Jet # and diameter (in)	Aerodynamic particle diameter (μm) [1]
Cyclonic Pre-cutter/1	cyclone	n.a.	60
Primary deposition plate/1	single jet	1 x 0.5	60
Stage 2	multi jet	12 x 0.0960	10
Stage 3	multi jet	90 x 0.0311	5
Stage 4	multi jet	110 x 0.0200	2.75
Stage 5	multi jet	110 x 0.0157	1.9
Stage 6	multi jet	110 x 0.0135	1.3
Stage 7	multi jet	105 x 0.0118	1
Stage 8	multi jet	105 x 0.0102	0.75
Stage 9	multi jet	78 x 0.0102	0.55
Stage 10	multi jet	56 x 0.0102	0.42
Stage 11	multi jet	40 x 0.0102	0.32

[1] The aerodynamic size ascribed to each stage was read out from the calibration table, for the actual sampling conditions (volumetric gas suction rate, temperature and cascade impactor configuration) and represent an ideal, spherical particle diameter with a uniform density of 1 g/cm^3.

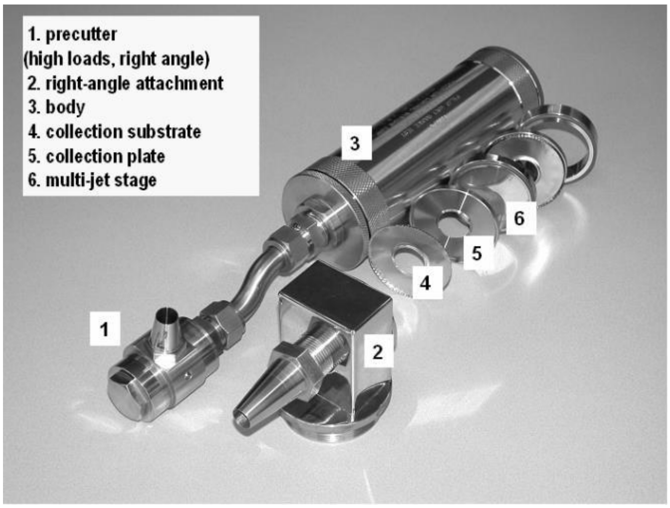


Figure 43. PILAT MARK V cascade impactor used by ECN part of TNO [142].

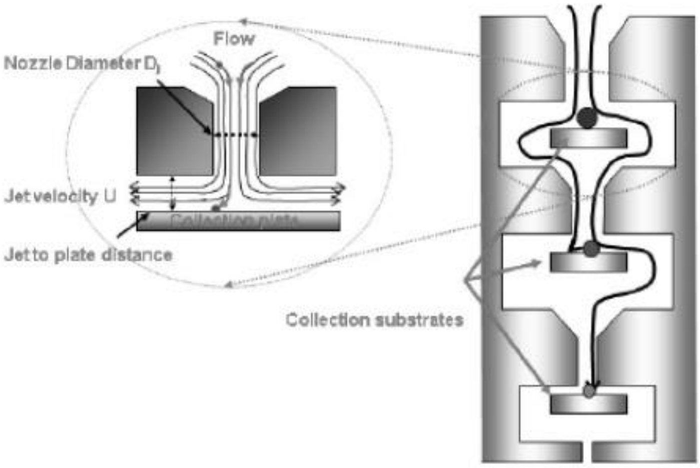


Figure 44. Schematic of gas and particles flow along the stages of the cascade impactor [141].

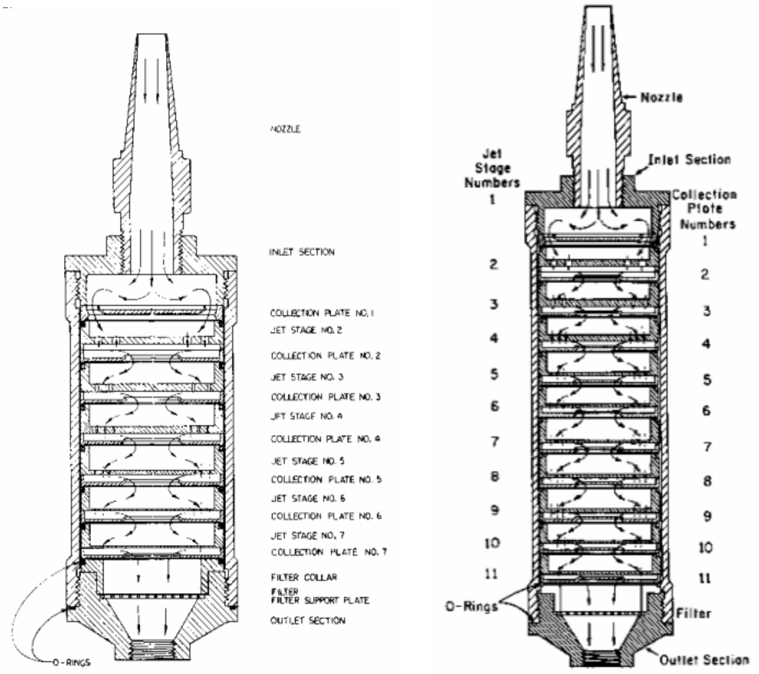


Figure 45. Cross-section of the MARK III (left) and MARK V (right) PILAT impactor [142].

After the gas sampling is complete, the weight of particulate matter deposited in each collection plate is measured (gravimetric analysis). From this, the particle size distribution of the particulate matter can be determined and plotted (fraction of particle size vs. concentration in gas in mg/Nm^3). Moreover, the collected dust can be further sampled and subjected to further analyses, such as SEM/EDX microscopy for combined qualitative morphology analysis and chemical composition; and elemental analysis, wet chemical analysis, ICP-OES, etc. for the chemical composition of the dust [69][142][143].

This impactor is used to classify particles in the range of 0.01 – 100 μm size. If it is expected that the gas will contain significant amounts of larger particles, a cyclone can be applied upstream in order to avoid the blockage of the impactor.

Two types of cascade impactors can be distinguished depending on the operating temperature: high-temperature impactors (HTI) and low-temperature impactors. The former operates at temperatures around 300-400°C. This temperature range is selected in order to avoid condensation of tars. However, this poses a technical challenge on the materials and equipment (high-temperature sealing, tracing for heating the impactor). Low-temperature impactors are operated at temperatures around 160-200°C. This makes gas sampling simpler. Another option to overcome the problem of tar condensation is the removal of tars in e.g. activated carbon, but this has the disadvantage of large losses of particles above 5 μm due to inertial impaction [143].

Figure 46 shows schematically how measurement of particulate matter using a high-temperature impactor is practically implemented by TU Delft. The probe used (5 mm internal diameter) is placed in the centre of the cross section of the gas duct and heated electrically (gas temperatures of 350-400°C until the cascade impactor). Upon starting of measurement, the high-temperature valve is opened, and the gas is sucked with a gas pump. A gas meter measures the total volume of gas sampled. The pump and gas meter are protected by a tar and water trap. A rotameter is used to regulate the gas flow in such a way that isokinetic conditions are ensured during the sampling.

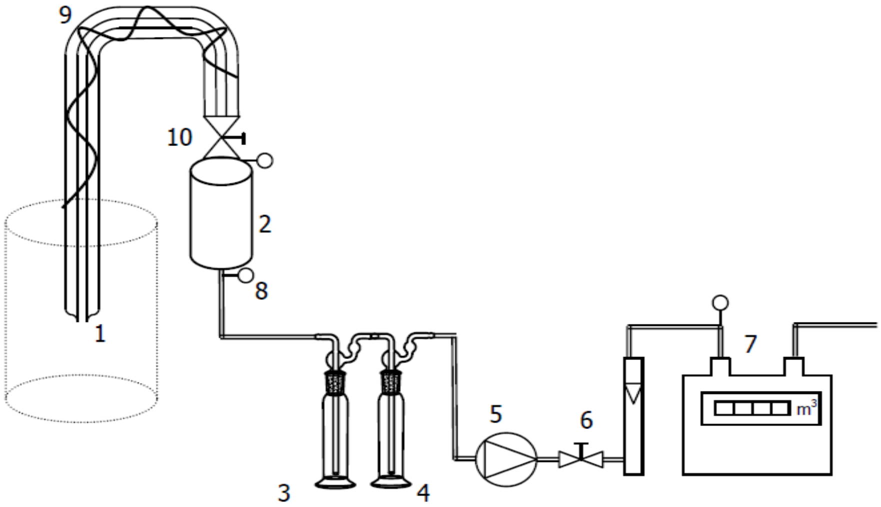


Figure 46. Implementation of measurement of particulate matter in gasifier setup using a cascade impactor by TU Delft [69]: 1. Sampling probe; 2. Cascade impactor; 3. and 4. Condenser and silica flask for trapping of water and tars; 5. Gas pump; 6. Rotameter for flow regulation; 7. Gas meter; 9. Electrical heating; 10. High-temperature valve.

Although the cascade impactor concept is relatively simple and straightforward, its operation requires some experience. The sampling time (which in turn influences the amount of dust sample collected from the gas) is an important operational parameter: if the amount of dust sampled is too low, there is a negative effect on the accuracy of the measurement (since the impactor needs a certain particle mass per stage to be able to measure the particle size distribution); on the contrary, overload of the device (thus, not proper trapping of the material in each stage) can be produced if a too long sampling time is applied. In the end, the sampling time is determined by trial and error [69].

As an example of application, a high-temperature impactor was used by BE2020+ and TU Graz within the BRISK project, where the high-temperature impactor was applied for the measurement of dust contained in product gas from a 100 kW$_{th}$ downdraft gasifier [69]. In this case, the sampling time was restricted to 3 minutes in order to avoid overloading of the impactor. The particles collected were further subjected to chemical analysis (CHNS, ICP-OES and ion chromatography) to determine the chemical composition of the individual particle size fractions.

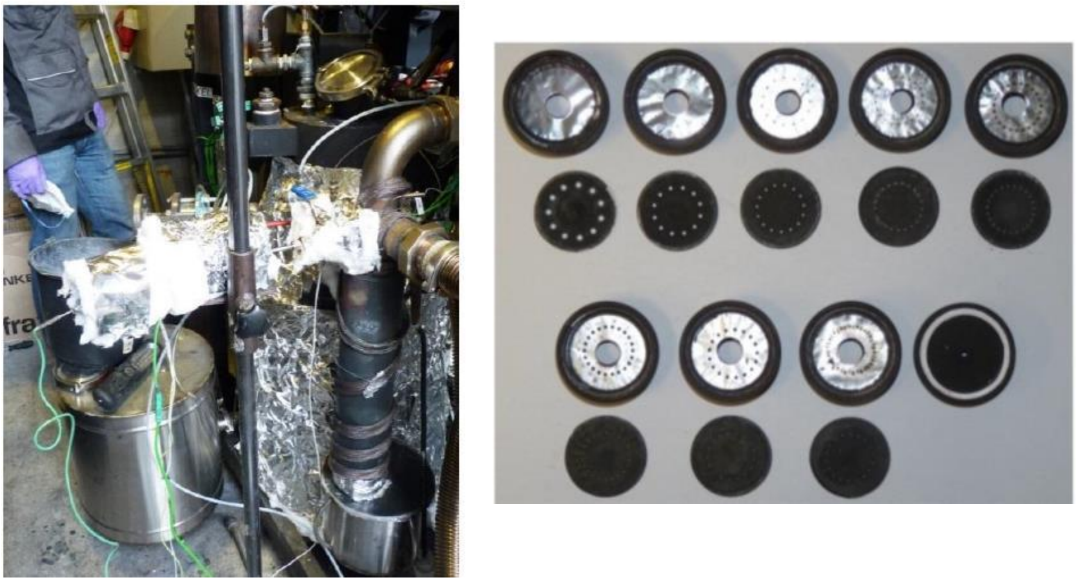


Figure 47. Implementation of high-temperature impactor in product gas line at TU Graz (left); loaded collection plates of high-temperature impactor after measurement (right) [69].

There are gasification processes (for example indirect gasification, circulating fluidized bed gasification operating under oxygen-steam conditions) in which the high amount of steam contained in the product gas is a challenge for particle measurement due to the higher risk of condensation during the gas sampling. TU Delft has developed a method for the measurement of particles from high-steam containing gases based on a Pilat Mark 5 cascade impactor. This equipment can measure size distribution of particles in the range of 0.3 to 20 μm diameter. The temperature in the sampling line is approximately 400°C in order to prevent condensation of tars and conversion of tar to particles (tar polymerisation to soot).

Low-temperature impactor was tested in gasification by the Abo Akademi University (Figure 48) in the framework of the BRISK project [69]. In this case, the sampling probe was located at the top of the gasification reactor, at a zone where the gas temperature was below 200°C. A cyclone was used upstream the impactor in order to remove larger particles (> 10 μm). Both the cyclone and the impactor were operated at 160°C (temperature selected to avoid condensation of sulphuric acid). The sampling time had to be reduced to less than 2 minutes in order to avoid overload of the plates of the probe. Figure 48 displays the aluminium plates (impactor stages) after the sampling of gas (with a cyclone implemented upstream). Here we can identify one of the main challenges of low-temperature impactors: the low gas sampling temperature leads to the condensation of tars, which stick to the plates (see lower row of pictures in Figure 48). This leads to blocking of the holes used to ensure the right flow velocity for particle separation, which in turn affects the accuracy of the results. The impactor has to be cleaned between each measurement to reduce this effect.

Figure 48. Stage plates of low-pressure impactor after sampling of particles from product gas at 160°C (Abo Akademi University, [69]).

Section 3.2.19 describes other examples of implementation of particulate matter at the Chalmers gasification pilot plant.

2.12.4 Scanning mobility particle sizer (SMPS)

A charged particle in an electric field experiences an electrostatic force. In an equivalent way as in a gravitational field, the particle in an electric field reaches a terminal electrostatic velocity when the force in the electric field is equal to the drag force. This property is used in the scanning mobility particle sizer (SMPS), where the particles are classified according to their electrical mobility and corresponding mobility equivalent diameter [141]. The basics of SMPS analysis can be found in Factsheet 36 of Document 2.

The theoretical measurement range of the aerosol spectrum is from 15 to 615 nm; hence, this apparatus is not suitable to measure coarser particulate matter load and can only be used in combination with other techniques. Furthermore, the apparatus is only suited for concentrations in the range up to approximately 3 mg/Nm^3 [142]. From the data measured by this technique it is possible to calculate total number concentrations as well as number concentrations per size class. Also surface and volume can be calculated from the data, but it is truncated by the given range. The number concentrations can be translated into mass concentrations, assuming a certain particle density.

Figure 49 shows the particle measurement system applied by Linnaeus University for the measurement of particulate matter from biomass gasifiers within the CHRISGAS project [143]. A dilution probe with nitrogen was firstly applied to quench the particle dynamics. In the dilution probe, the sample was diluted with preheated N_2 and the gas temperature was reduced to approximately 300°C. Then, an activated carbon bed was placed for the removal of tars. Downstream bed of granular activated carbon, a cyclone or filter (not shown in the figure) was used, and an ejector diluter was applied to further dilute the gas with pressurized air. The gas was then split between a number of instruments:

- The CO infrared analyser was used to adjust and determine the dilution ratio.

- A scanning mobility particle sizer (SMPS), including a differential mobility analyser and a condensation particle counter, was used to determine the number size distribution of particles with mobility equivalent diameters in the range of 10-670 nm.

- An aerodynamic particle sizer (APS) was used to determine the number size distribution of particles with an aerodynamic diameter of 0.5-20 μm.

- A low-pressure impactor (LPI) with a d_{50} of 0.030-10.33 μm aerodynamic diameter for stages 1-13 was used for the particle mass size distribution.

All particle mass size distributions and particle mass concentrations measured are then corrected for dilution in the sampling system.

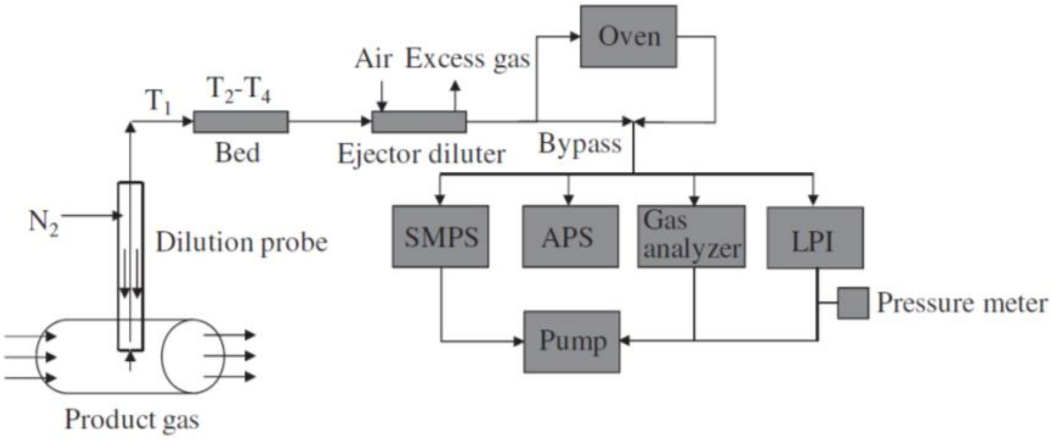


Figure 49. Schematic implementation of particle measurement system in CFB and indirect BFB by Linnaeus University [143].

2.12.5 In-situ soot diagnostics: laser-induced incandescence (LII)

Another quite elegant option for particle measurement, specifically aiming at soot particles in the nanometre size range (thus, particularly suitable for entrained-flow gasification processes), is laser-induced incandescence (LII), currently under development by DLR, which is described in more detail in Factsheet 24 of Document 2. This technique is applied for non-intrusive online measurements of soot particle characteristics such as soot volume fraction or primary particle size, and it is therefore useful to resolve transients of reactor operation. Applications both inside combustors or after sampling from the exhaust system of technical combustors are known, although the application to gasification is still scarce and therefore limited to a small range of operation. While the advantages of this diagnostics for process control are evident, the requirements are demanding: it requires optical access, relatively expensive laser and detection equipment and skilled personnel for operation and data evaluation. Figure 50 shows as an example results from LII experiments at the Research Gasifier REGA at KIT. The image shows the laser excited region featuring a homogeneous particle distribution (blue) the shaded circular aperture of the optical water-cooled probe and the schematic of a process thermocouple shielding part of the emitted LII signal. For further details on the experimental setup, please refer to Section 3.2.14.

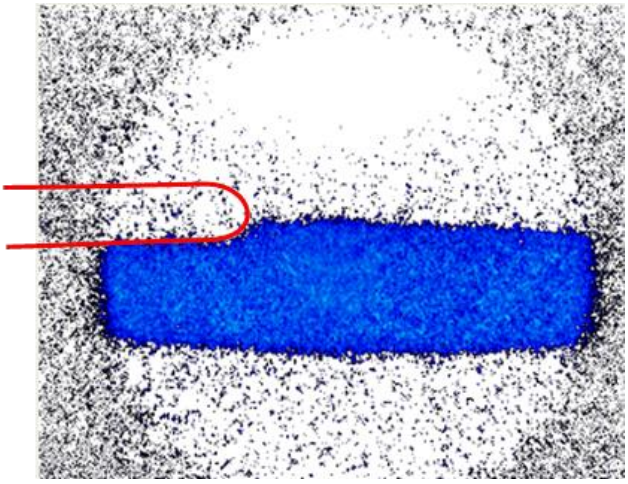


Figure 50. Time-averaged visualization of particle distribution inside the Research Gasifier REGA at KIT using laser-induced fluorescence (LII) [144].

A diode-laser-based system for extinction measurements of soot content developed within the Swedish Gasification Centre is described in Section 3.2.21.

3. Practical implementation of gas analysis at industrial and research gasification plants

3.1 INTRODUCTION

One of the main advantages of (biomass) gasification is the broad range and versatility of applications of the product gas, which can be used for the production of heat, power and mechanical energy (in boilers, gas engines, gas turbines, etc.), or as feedstock for the production of fuels and chemicals (for example, for synthesis of methanol, ethanol, Fischer-Tropsch liquid fuels, Synthetic Natural Gas, etc.). The final application of the gas will not only influence the design and selection of the most suitable gasification and gas upgrading technologies, but also the needs and challenges of gas analysis in the gasification plant. The specific application of the product gas (heat/power, biofuels/chemicals synthesis) will determine the range of target gas compounds (for example, if nickel catalysts will be used, sulphur compounds will be needed to be monitored), and the required measurement detection limits (thus, the cost of the analysis). Moreover, special requirements are posed when applying gas analysis in an industrial environment: in this case, factors such as robustness and cost (at the cost of lower precision) and safety considerations play an important role when selecting the most suitable gas analysis technique. With this background, this chapter compiles several representative examples of experiences from industrial- and pilot plants, and lab-scale setups that illustrate the different needs for gas analysis. The examples shown in this report try to cover as wide as possible a range of scales, gasification technologies and applications of the produced gas.

3.2 IMPLEMENTATION OF GAS ANALYSIS – PRACTICAL CASES

3.2.1 Gasification for heat production – The Amer 9 plant

The Amer co-firing coal power plant (Geertruidenberg, The Netherlands, see Figure 51) consists of unit 8 (645 MW_e, in operation from 1980 to 2016) and unit 9 (600 MW_e, in operation since 1993) [145]. Besides coal, biomass is indirectly co-fired in the Amer 9 plant. Demolition- and waste wood (100000 ton/y, equivalent to 85 MW_{th} [146][147]) is gasified in a circulating fluidized bed gasifier. After cleaning, the resulting product gas is co-fired in the boiler of unit 9. In a 3-phase plan recently announced, coal will be gradually replaced with biomass (from 35% biomass in 2018 to 80% biomass in 2019) [148].

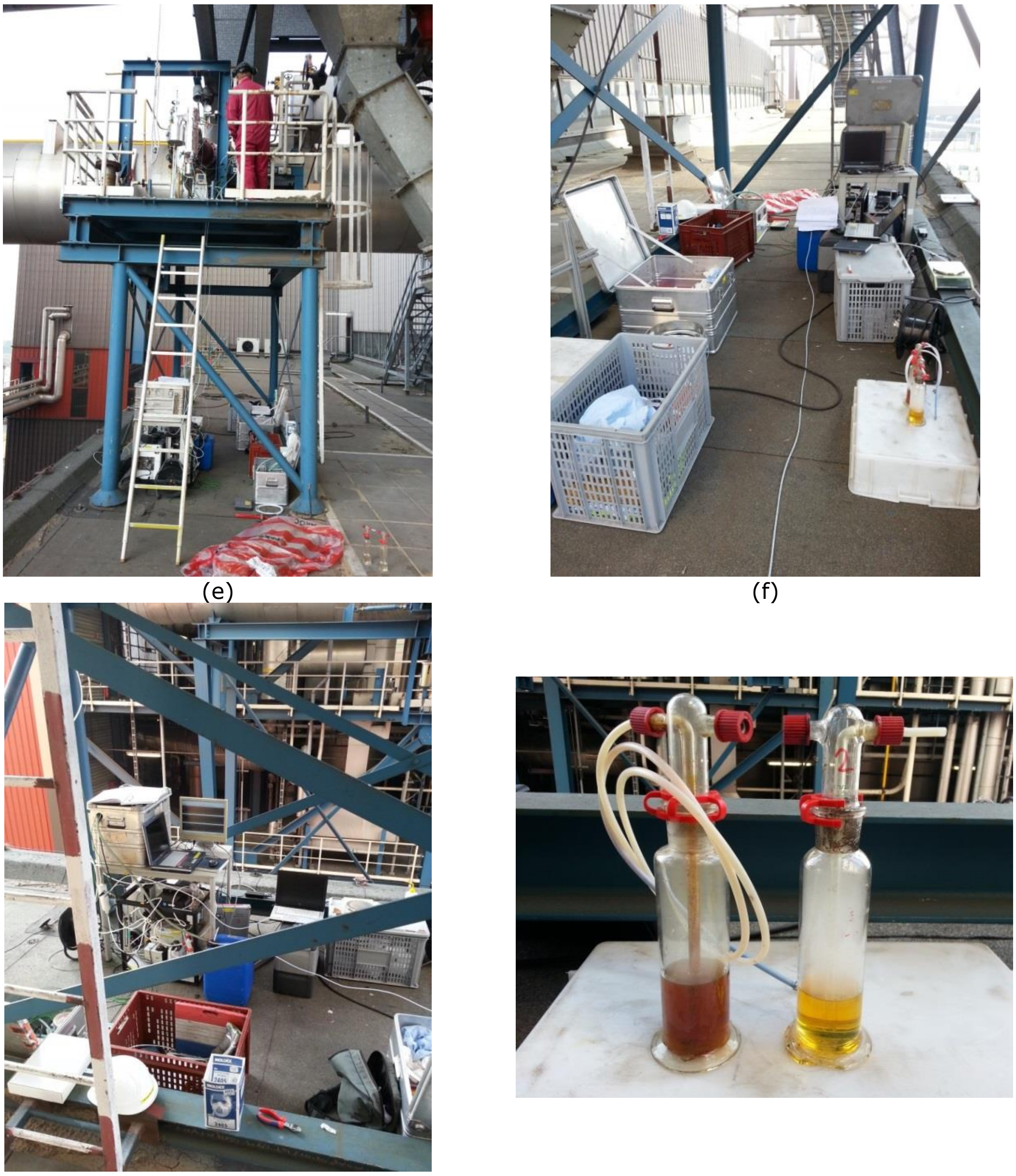
Figure 51. Amercentrale 9 power plant (picture: ECN part of TNO).

When the product gas is combusted in a boiler, a very important property of the product gas is its heating value (moreover, it has to be ensured that the plant complies with emission limits). The gasification unit in the Amercentrale included during its first operation period online gas sampling for gas analysis using gas chromatographs (located in a container in the gasifier building). Eventually, the continuous gas sampling was stopped due to blocking by solids and condensing tars. Since then, the gas analysis actions were reduced to individual actions every couple of years. This could be done because an indirect, online calculation of the energy content of the product gas (energy balance) was possible, based on the fuel energy input and the steam production of the boiler. For monitoring the emissions, dust concentration measurement and gas flow measurement are applied. All operational daily measurements and related calculations are validated every couple of years by dedicated measurement campaigns [149].

One of these dedicated measurement campaigns at the Amercentrale gasifier was performed by ECN part of TNO in March 2014 in the framework of a national TKI project. Figure 52 shows some pictures of the implementation of gas analysis (product gas composition and wet chemical analysis for determination of chlorine and heavy metals). The measured heavy metal content was determined to be approximately 19 mg/MJ, a value below the maximum amount of 30 mg/MJ stated as quality criterion by Dutch regulations.

(a) (b)

(c) (d)



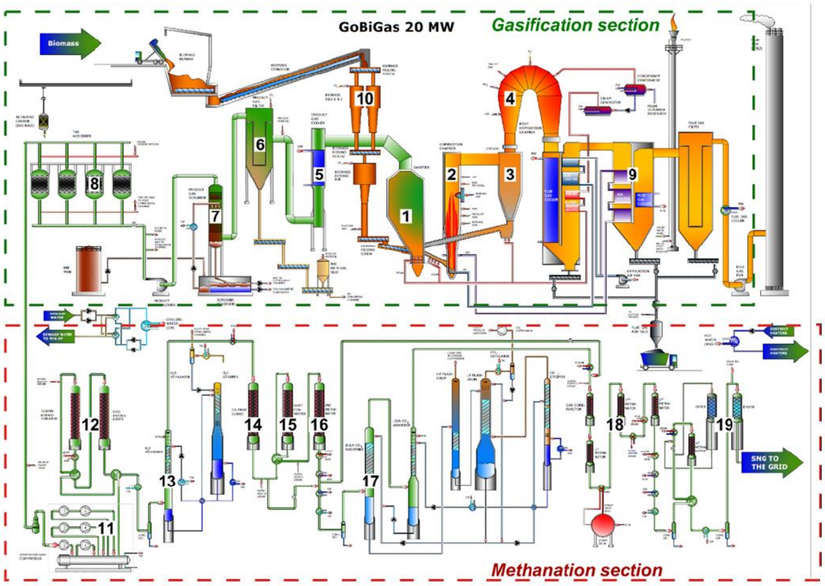
(e) (f)

(g) (h)

Figure 52. Measurement campaign at the Amercentrale gasifier: (a) product gas line, with gasifier in the background; (b) gas sampling; (c) and (d) location of measurement probe, and gas pre-sampling system at the probe; (e), (f) and (g) gas analysis equipment; (h) impinger bottles after wet chemical gas analysis (sampling of Cl and heavy metals). Pictures courtesy of ECN part of TNO.

3.2.2 Gasification for production of Synthetic Natural Gas – the GoBiGas plant

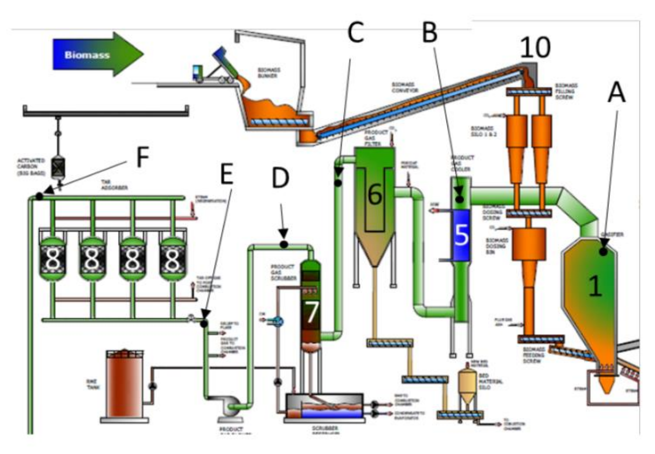
The GoBiGas plant (32 MW_{th} thermal input, 20 MW_{th} SNG output), located in Gothenburg (Sweden), is the first commercial plant for production of biomethane from biomass gasification [150][151][152]. Figure 53 shows a schematic diagram of the process. FICFB (Fast Internally Circulating Fluidized Bed) indirect gasification technology is applied using wood chips as gasification feedstock. Tars are removed in an oil scrubber, after which 2 beds of activated carbon remove BTX. The clean product gas then enters the gas upgrading (H_2S removal, olefin hydrogenation, WGS) and methanation train. The product is substitute natural gas (SNG) that is injected to the gas grid. Despite the successful technical achievement, the plant has been recently mothballed [153].



1. Gasifier
2. Combustor
3. Cyclone
4. Post Combustion Chamber
5. Product Gas Cooler
6. Product Gas Filter
7. RME-Scrubber
8. Adsorbent beds
9. Flue Gas Train
10. Lock hoppers
11. Compressor
12. Olefin hydrogenatio
13. H_2S Scrubber
14. Guard bed
15. Water Gas Shift Reactor
16. Pre-Methanation
17. CO_2 Scrubber
18. Methanation
19. Dryers

Figure 53. Schematic of GoBiGas plant [60].

Table 20. Overview of gas sampling points at GoBiGas plant [60].

Measurement point	Location in plant	Scheme
A	Gasifier freeboard	
B	Before product gas cooler	
C	After product gas filter	
D	After RME scrubber	
E	Online product gas analyser (reference)	
F	After activated carbon beds	

Recently, a new gas and tar sampling system was implemented at the GoBiGas plant in order to improve the evaluation of the plant performance and thus to optimize the process [60]. The system allowed the parallel connection of different analysis equipment, as well as to switch between different measurement points around the plant (summarized in Table 20). The gas analysis at the different positions made possible to assess the dynamic performance of a number of important units: the gasifier, the gas cooler, the product gas filter, the RME scrubber and the activated carbon beds.

Figure 54 displays the schematics of the new gas sampling system implemented at GoBiGas. The gas sampling line from point B is traced at 350°C, whereas points C and D are traced at 200°C to avoid tar condensation. The gas sampling system has been operational for more than 500 hours.

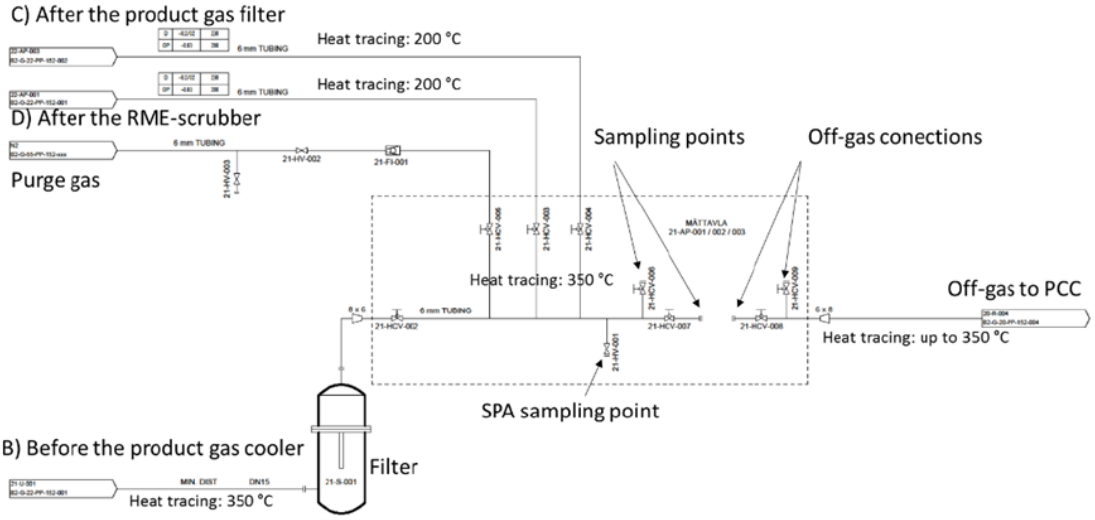


Figure 54. Schematic layout of new gas sampling system implemented at the GoBiGas plant [60].

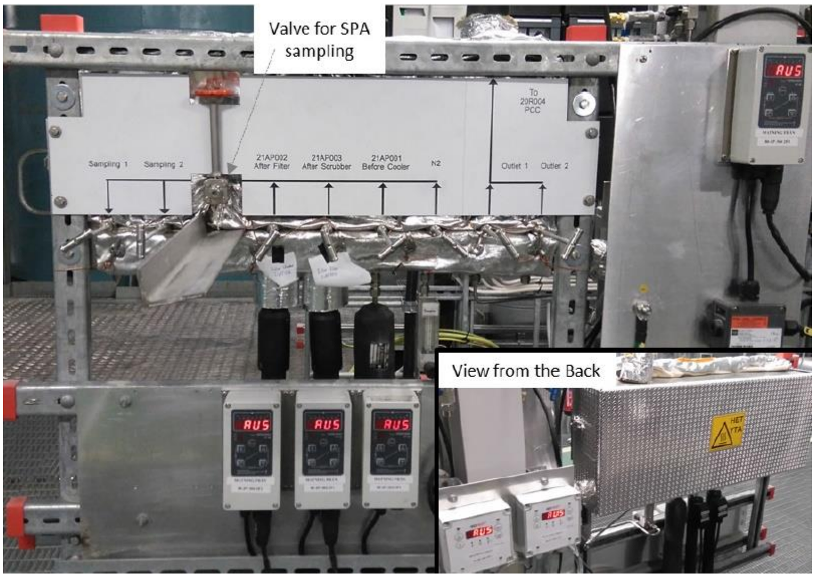


Figure 55. Central panel of new gas sampling system implemented at the GoBiGas plant [60].

Since the closer to the gasifier the sampling point is located, the more challenging is the measurement (hot gas containing tars, particles, and alkali compounds), there is a trade-off between the acceptable complexity of the measurement and the information that can be obtained. In order to enable measurement of product gas before the cooler (gas temperature at 650-850°C), a temperature-controlled sampling probe was designed. The gas probe keeps the gas above 300°C (to avoid tar condensation) but below 350°C (to ensure condensation and thus removal of alkali salts). The cooling medium used is superheated steam, a readily available stream at the plant which moreover allows direct venting to the product gas. The temperature of the sampled gas can be controlled by adjusting the steam flow. The sections not cooled with steam are electrically traced and insulated to avoid cold spots. A high-temperature ceramic filter is placed to remove soot and alkali particles. The gas flow in the probe is up to approximately 10 NL/min [60]. Since attrition of the probe under the challenging sampling conditions was an issue, 2 coatings (ZrO_2 and Al_2O_3/TiO_2) were applied externally to the probe.

The new gas sampling system was used to conduct a number of measurements: particles and alkali compounds, BTX and tar, and permanent gas compounds. The analysis method developed by Gothenburg University was tested for online measurement of alkali compounds, particles and heavy tars during the start-up and steady operation of the GoBiGas plant [126]. In total more than 60 hours of real-time measurements were performed. The authors report that during some of the measurements, the sampled gas flow was influenced by cyclic pressure fluctuations (period of 3 minutes) inside the gasifier. This resulted in some measurements with high uncertainty (> 5000 dilution factor), which had to be discarded from data analysis. However, the high resolution of CO concentration measurement made possible to correct for rapid variations in the dilution ratio. Besides the gas-phase analysis, XRD analysis was applied to the deposits formed at the inlet of the product gas cooler (out of the scope of this report).

Both offline- (SPA analysis) and online (CON-TAR) methods were applied for BTX measurement. SPA was selected compared to tar guideline due to the fact that it allows safe and convenient sampling (no hazardous solvents required), thus more appropriate for application in large plants with strict safety regulations. Besides SPA, an alternative sampling approach was tested at position B (before gas cooler), similar to SPA, but using a long and narrow probe. Additionally, a prototype of the CON-TAR online analyser of tars developed at Technical University of Berlin was connected and tested for more than 400 hours. Please refer to Section 4.3 for more details about the performance of the prototype.

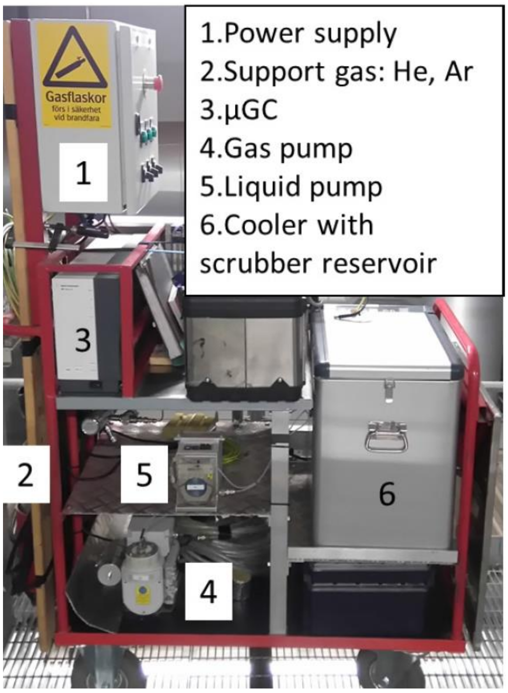


Figure 56. Portable micro-GC unit used at the GoBiGas plant [60].

Permanent gas composition was evaluated with a gas monitor set (CO, CO_2, CH_4, H_2, and O_2), and portable micro-GC analysis (H_2, CO, CO_2, CH_4, He, C_2H_x, C_3H_x, H_2S, COS, SO_2, benzene, toluene, phenol and water, Figure 56). The micro-GC columns included a COX, PPU and Wax. Therefore, separation of N_2 and O_2 (air components) was not possible. A PPQ would have been necessary, but this type of column was not suitable for measurement at large scale (it is more sensitive to water, and therefore it requires more frequent regeneration and recalibration) [60].

3.2.3 Gasification for production of Synthetic Natural Gas – The GAYA platform

The R&D GAYA project aims at developing an innovative, competitive and sustainable pathway to produce bio-SNG from dry biomass thermochemical conversion. To prove the economic, technical and environmental relevance of this pathway, a consortium led by ENGIE (formerly GDF SUEZ) and gathering expertise from various industry, academic and private research centres was created in 2010 [154].

One of the main assets of the project is the construction of a semi-industrial demonstration plant located in Saint-Fons, near Lyon (France). The GAYA R&D platform (400 kW_{th} SNG output) is designed to produce bio-SNG from lignocellulosic biomass gasification (Figure 57 (a)). Gasification is performed in a FICFB (Fast Internally Circulating Fluidized Bed) reactor. Then, a series of low-temperature gas cleaning technologies eliminate trace components from syngas, namely scrubbers to remove heavy tars, and adsorption to capture light tars as well as inorganic compounds such as hydrogen sulphide or ammonia. Finally, the purified syngas is converted into synthetic natural gas (SNG) through a fluidized-bed catalytic methanation reactor developed by ENGIE.

This experimental platform is a powerful tool to provide feedback and quick wins for the industrialization. Optimal operating conditions are explored for specific technologies to increase the carbon conversion into bio-SNG and the process availability. Furthermore, given its size, the project will help validate the distributed control system and identify possible monitoring simplification. The know-how developed during the commissioning and the start-up phases, and the demonstration of gasification of different types of biomass feedstock will also contribute to significant reduction of the bio-SNG production costs. In addition, the research program plans to improve the environmental benefits and to lower the bio-SNG production costs through the tests of alternative technological configurations made possible thanks to the flexible design of the platform [155].


(a) (b)

Figure 57. The GAYA platform (a) and the R&D shelter for online gas measurements (b). Pictures courtesy of ENGIE Lab CRIGEN.

As part of the R&D program at the GAYA platform, it is necessary to accurately characterize the quality of the gas all along the process, from the raw syngas to the bio-SNG product. As such, the adopted strategy was to rely as much as possible on online gas sampling and analysis. This strategy includes 7 sampling points located on the process. On each sampling point, heated filters and transfer lines enable to deliver the gas sample to a shelter where a multiplexing system measures the samples (Figure 57 (b)). This detailed analysis allows the full characterization of each step, which is the basis for the optimization work of the process parameters. Five heated sampling boxes on syngas and bio-SNG (Figure 58 (a)) are collected on a heated box (Figure 58 (b) and (c)). Automatic stream selectors enable to select the desired sample to analyse. Moreover, two sampling lines are dedicated to flue gas characterization (downstream and upstream the dust filter).

The gas samples are analysed on 8 different online devices (Figure 58 (d)): 2 dedicated for flue gas measurements, and 6 focused on syngas and bio-SNG analysis. First, micro-GC equipped with thermal conductivity detector (TCD) is used to measure light tars such as BTEX, nitrogen and carbonyl sulphide (COS). Then a set of 4 laser spectroscopy OF-CEAS devices (see Factsheet 31 in Document 2) is used to measure permanent gases (CO, H_2, CO_2, CH_4, H_2O and O_2) and inorganic trace compounds (NH_3, H_2S and HCl) [156]. Finally, Flame Ionization Detector (FID) allows to determine the total hydrocarbons content. FID and UV-fluorescence equipment are also used to measure total hydrocarbons and SO_2 in flue gas, respectively.

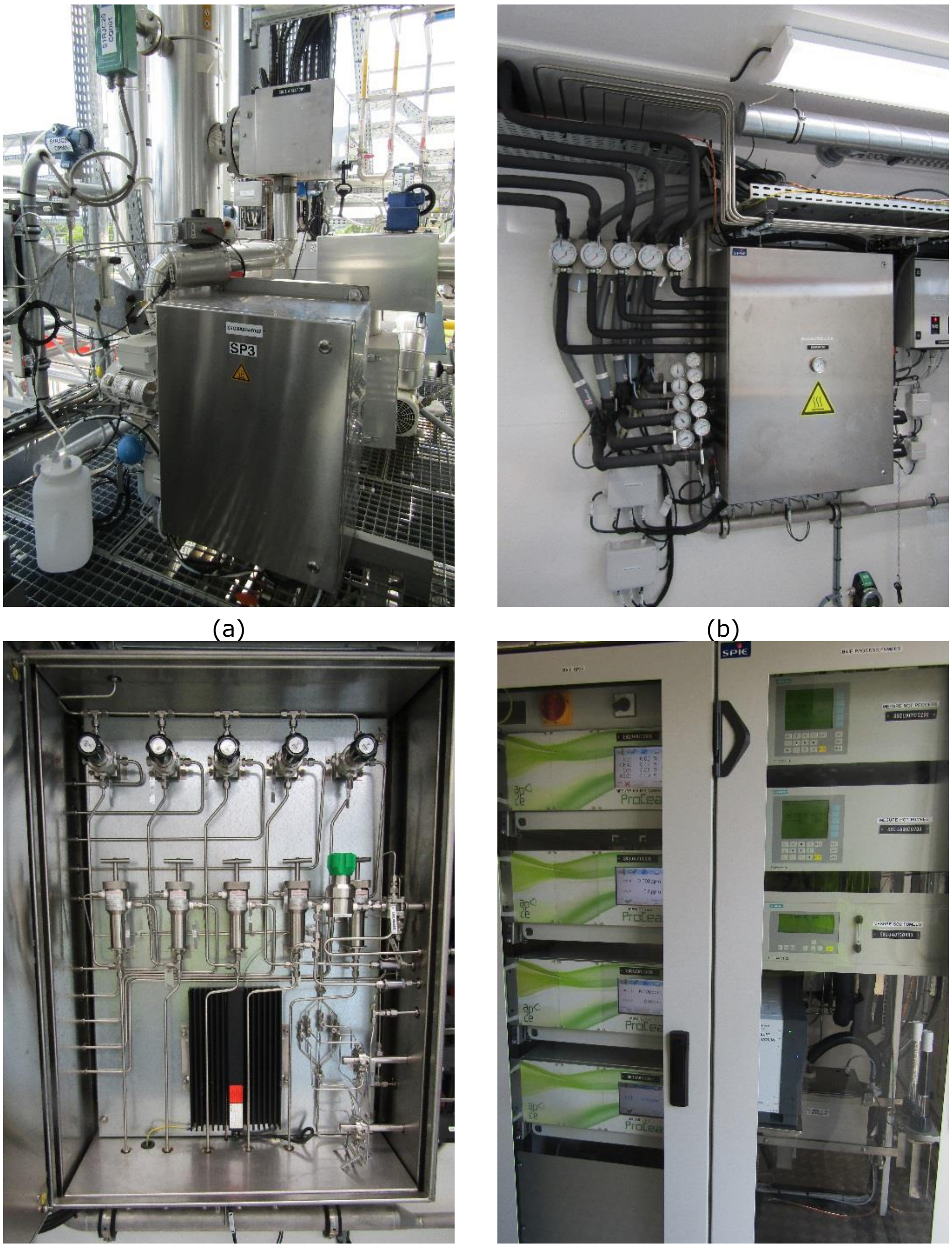

(a) (b)
(c) (d)

Figure 58. Gas analysis equipment at the GAYA platform. Picture courtesy of ENGIE Lab CRIGEN.

In addition, offline methods are employed mainly for tar measurements, biomass or condensate characterization. These offline techniques are used when online measurements are not available or too expensive, or when online quantification limits are too high. For example, specific methods using a pre-concentration step (tar protocol or Solid Phase Adsorption) are applied by ENGIE Lab CRIGEN for tar sampling. The tar protocol sampling is suitable for high level of tars (e.g. upstream tar adsorbers) whereas the sampling system by solid phase adsorption (SPA) and thermal desorption is suitable for low level of tars in purified gases (e.g. downstream tar adsorbers). The SPA technique leads to quantification limits of 1 µg/m^3 (ppb level in gas). In addition, SPA is an easy-to-use technique which matches well with onsite constraints because does not require any solvent.

In the laboratory, the use of liquid injector or thermal desorption unit (TDS) and a gas chromatograph coupled with a flame ionization detector (GC-FID) and a mass spectrometer (GC-MS) enable to characterize all samples from raw to final product gases. Thanks to the use of these two specific detectors, the analytical method enables the identification and quantification of the components in a sample (Figure 3).

Figure 59. Thermal desorption unit coupled with GC-FID/MS. Picture courtesy of ENGIE Lab CRIGEN.

In the case of complex samples (e.g. raw product gas or condensates), the potential of two-dimensional gas chromatography (2D-GC) was also tested by ENGIE Lab CRIGEN in collaboration with ESPCI Paris Tech. Target compounds include aromatics hydrocarbons such as benzene, and naphthalene; and heteroaromatic organic compounds such as phenol, thiophene and derivatives from these compounds. 2D-GC is an analytical technique that overcomes the limitations of one-dimensional gas chromatography (for example, co-eluted components). 2D-GC enables to carry out comprehensive analysis in order to improve diagnostics for process performance and risks management (Figure 60) [81].

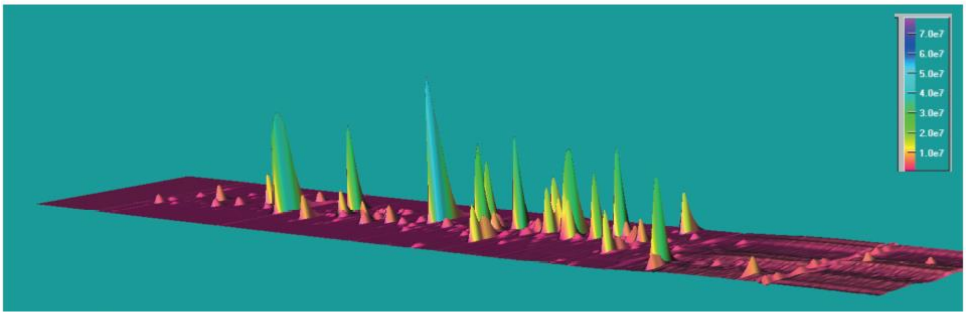


Figure 60. 3D-chromatogram obtained by ENGIE Lab CRIGEN and ESPCI Paris Tech from product gas from an agricultural biomass [81].

3.2.4 CHP production - Gas analysis at the Güssing, Oberwart and Villach plants

In Austria there are 3 combined heat and power plants, located in Güssing, Oberwart and Villach which apply FICFB indirect gasification technology (in which 2 gas streams – product gas and flue gas- are generated). The product gas, once cleaned, was combusted in gas engines for the production of electricity and heat. Table 21 summarizes the technical features of the CHP plants. Figure 61 shows as an example the schematic of the Güssing plant (the other 2 plants having a similar scheme process). These CHP plants are currently on hold.

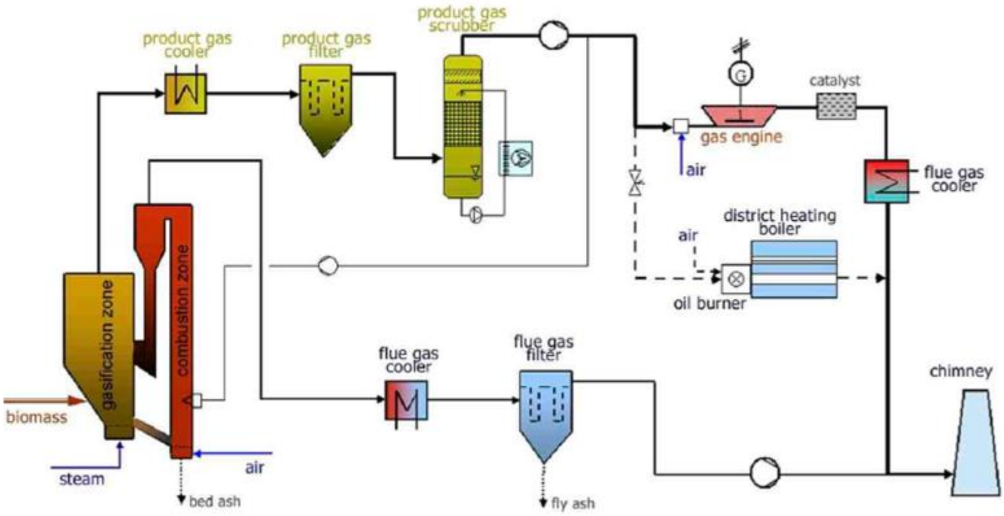


Figure 61. Schematic layout of Güssing CHP plant [110].

The following gas analysis techniques were implemented at the Güssing plant [158]:

- Gas chromatography for the permanent gases in the product gas.
- Flue gas composition (including CO, NO_x, SO_x, and PAH), both at the combustion side of the gasifier, and at the outlet of the gas engine.
- Guideline method for measurement of tars and particles, but using toluene instead of iso-propanol as solvent.
- Hydrocarbons / tar content in solvents (e.g. tar content in rapeseed methyl ester, RME).
- Complementary to gas compounds, analysis was applied to bed material and ashes (activation of the bed material).
- GC-SCD applied to gas bags for measurement of sulphur compounds.
- Wet chemical analysis for sampling of Cl, NH_3 and HCN (analysis with ion chromatography).
- GC analysis (online or applied to gas bags) for measurement of BTX and naphthalene.

In the plant, fast analysis was necessary and thus online systems (infrared, paramagnetic) were implemented for the measurement of gas components. The main challenge reported for gas analysis was to clean the gas and to take it to the analyser with good availability. Complementary to gas compounds, the analysis of the engine oil provided also information about the performance of the gas cleaning section [158]. In general, the gas analysis techniques applied at the plant, although reliable, were considered too expensive or entailing too much maintenance. Güssing was also extensively used as demo plant for the setup of different trains for production of biofuels. In this case, the challenges include the different species of interest compared to CHP, and the need for lower detection levels (ppb instead of ppm) [158].

Wolfesberger-Schwabl from TU Wien [110] performed several measurement campaigns for the comparison of the product gas composition, tar content and composition and inorganics measurement from the 3 dual fluidized-bed steam gasification CHP plants located in Austria. In all cases, tar was sampled at different plant locations.

Table 21. Overview of features of Austrian CHP plants where measurement campaigns were carried out by TUV for the measurement of tar, H_2S and NH_3 [110].

	CHP Oberwart	**CHP Villach**	**CHP Güssing**
Capacity (MW_{th})	8.6	15	8
Start operation	2007	2011	2002
Fuel	Wood chips	Wood chips	Wood chips
Bed material	Olivine (CaO as additive)	Olivine (CaO as additive)	Olivine (dolomite as additive)
Gasification T (°C)	835-865	850	870
Combustion T (°C)	900-940	920	910
Energy production	Gas engine District heating	Gas engine District heating	Gas engine District heating
Tar sampling points [110]	After gasifier / after filter/ after scrubber	After gasifier / after filter/ after scrubber	After filter

3.2.5 Entrained-flow gasification for biofuel production - the Bioliq® pilot plant

The Bioliq pilot plant located at the KIT North Campus in Karlsruhe (Germany) is a research platform for the production of synthetic fuels and chemicals from biomass [150]. Bioliq uses high-pressure entrained flow gasification (EFG). The slurry fed, oxygen / steam blown entrained flow gasifier has been designed for pressures up to 80 bar and a fuel throughput of up to 1 ton/h. The system is designed to utilize fuels with calorific values in the range from 13 to 25 MJ/kg. The gasification chamber is equipped with a SiC-lined, water-cooled membrane wall particularly suited for the conversion of ash-rich feedstock. The downdraft gasifier flame reaches temperatures of 1200– 1600°C well above the ash melting point. A typical dry syngas composition from the Bioliq gasifier is: 27 – 39 vol.% H_2, 27 – 39 vol.% CO, and 14 – 28 vol.% CO_2. Methane is normally below 0.1 vol.%. The difference to 100 vol.-% is nitrogen that is used for purging.

The Bioliq EFG has been in operation since 2013. Since then, 700 ton of suspension (a liquid slurry of pyrolysis oil and char) fuel have been gasified since. The gasifier is operated 24/7 in campaigns of 2 to 4 weeks [159].

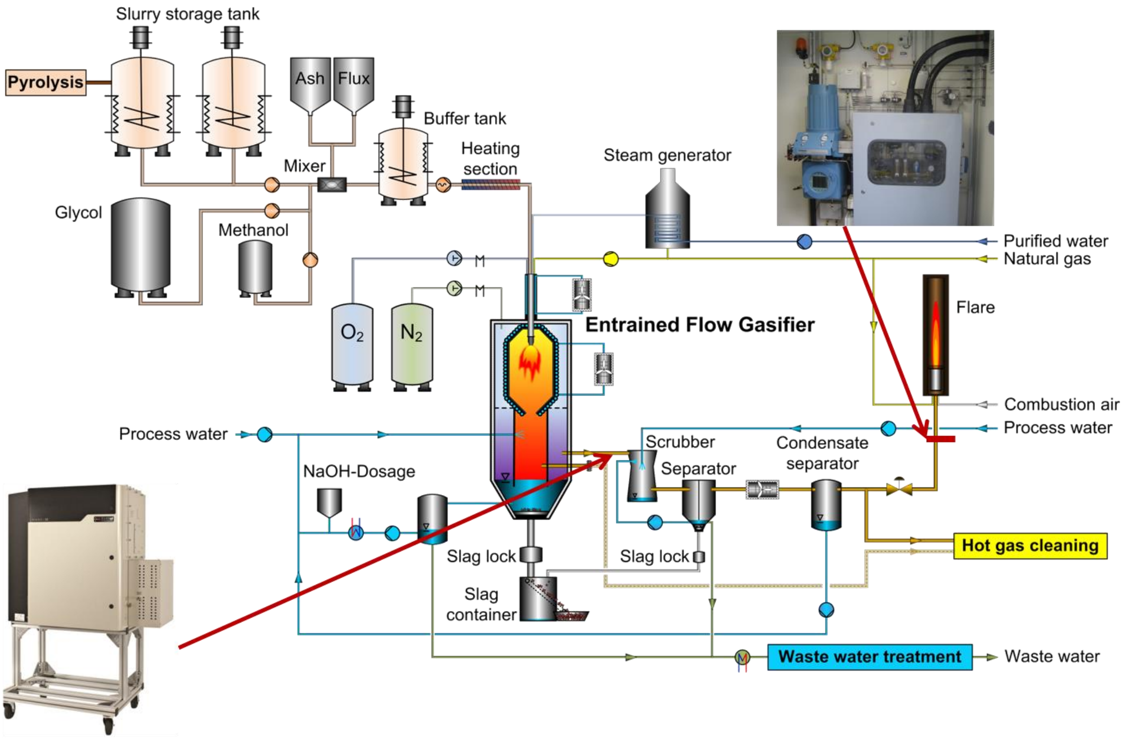


Figure 62. Flowsheet of Bioliq entrained flow gasifier pilot plant with sampling points for gas analysis [159].

Figure 62 displays a schematic of the pilot plant, including the points for gas analysis. Because of the high gasification temperature (>1200°C), the measuring of tar is not of great importance. There are 2 sampling points with filter and pressure release that are provided with a mass spectrometer and a process gas chromatograph with syngas to measure permanent gases. The syngas is analysed after the quench after condensation by a process GC-TCD (Figure 63), and by a quadrupole mass spectrometer (Figure 64) [159].

Figure 63. Gas chromatograph used at the Bioliq plant by KIT [159].

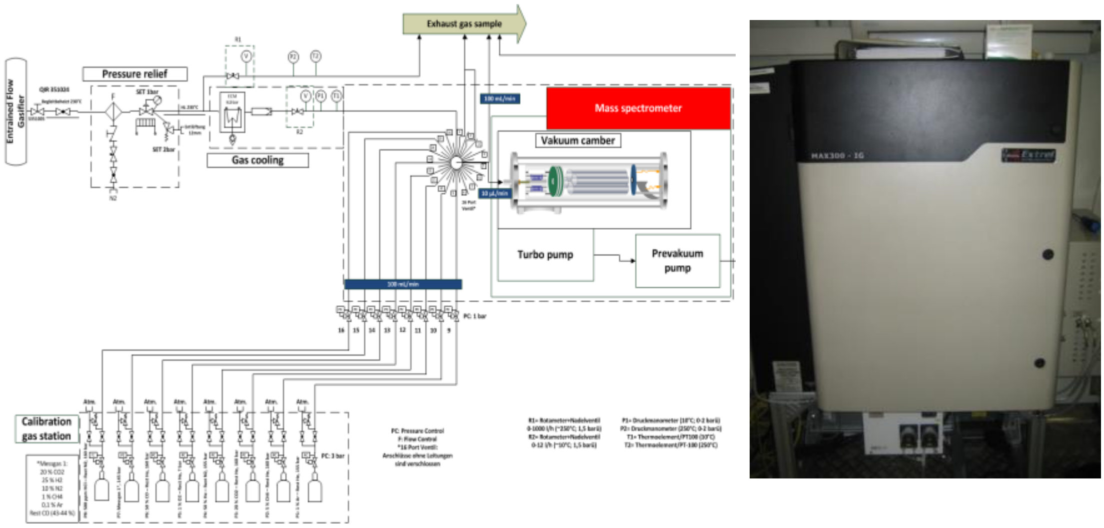


Figure 64. Mass spectrometer used at the Bioliq plant by KIT: schematic setup and picture [159].

3.2.6 Low-temperature gasification - 100 kW LT-CFB and 6 MW Pyroneer gasifier (DTU)

Technical University of Denmark (DTU) performed several measurement campaigns in the period 2012-2014, at the 100 kW LT-CFB gasifier (Campus Risø, DTU) and at the 6 MW Pyroneer gasifier (Asnæsværket, Kalundborg, Denmark) [65], both of them low-temperature processes.

Product gas from the LT-CFB gasifier was sampled using gas pipettes, impinger flasks and the Petersen column for offline measurements. Impinger flasks were used for ammonia and nitrogen measurements. Additionally, in-situ/online spectroscopy methods were applied for the online measurement of phenol and naphthalene. In June 2017, some in situ far-UV measurements on the product gas from the high-temperature Viking gasifier have been done with focus on Cl-compounds. Later in November 2017, far-UV spectroscopy was applied for in-situ Cl-compounds measurements on the LT-CFB gasifier. Figure 65 displays the implementation of in-situ FTIR at the Pyroneer gasifier [11][34], whereas results from optical measurements (UV spectroscopy) for in-situ tar analysis are shown in Figure 66.

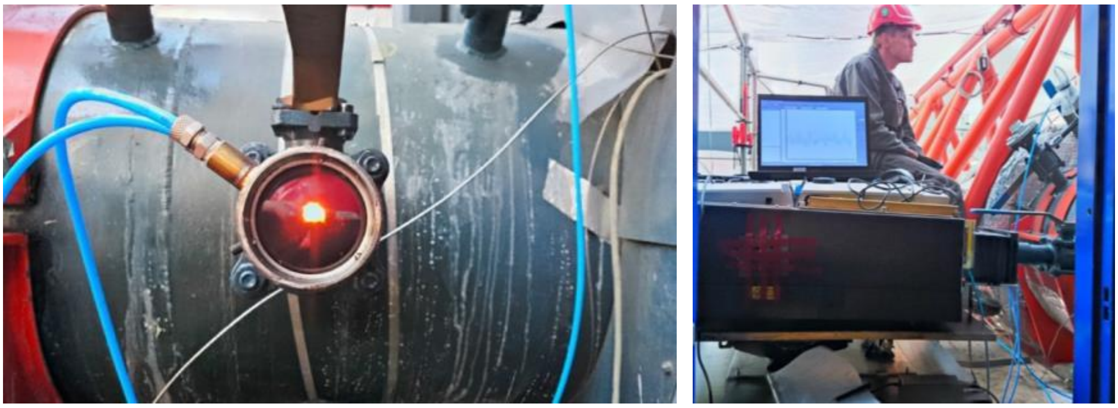
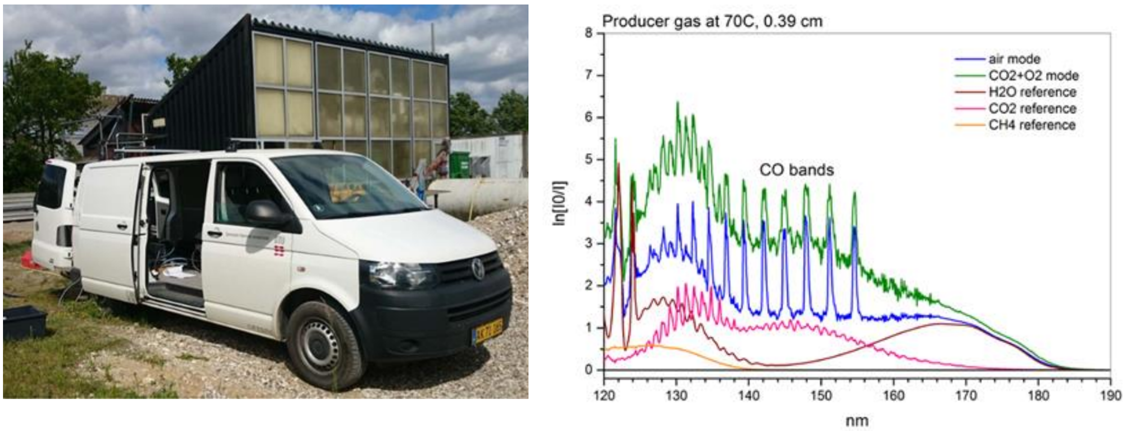


Figure 65. FTIR absorption measurements by DTU at the LT-CFB Pyroneer gasifier [11].



(a) (b)

Figure 66. Optical measurements applied at the Viking gasifier by DTU [122].

Figure 67 compares results of UV absorption measurements obtained at the Viking and LT-CFB gasifiers. The absorption at wavelengths above 190 nm in the gas from the LT-CFB indicates a higher content of BTX and tar, and more NH_3. CH_3Cl was also detected in the gas.

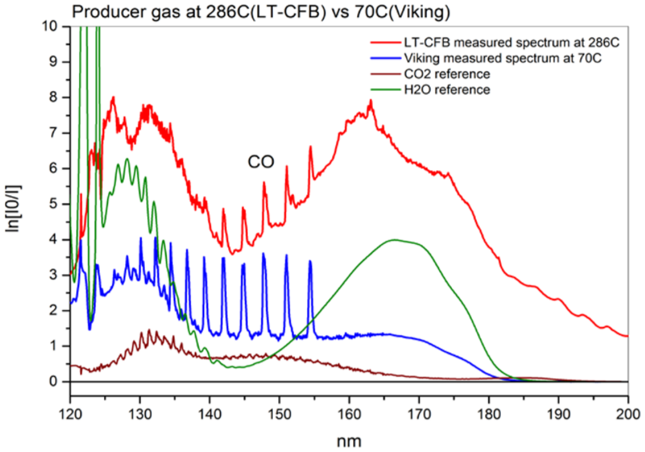


Figure 67. Comparison of optical (UV absorption) in-situ measurement of product gas from Viking (70°C) and LT-CFB gasifiers [122].

3.2.7 Waste gasification – the Tondela plant

Woody biomass is in general a relatively clean fuel. It contains low content of S, N and Cl, although the ash content might pose a technical risk in some cases due to the ash composition (e.g. high content of alkali metals). Therefore, in general, the concentration of the derived S-, N- and Cl-compounds is expected to be quite low (in the range of ppm level) in the product gas generated in the gasification process.

However, waste is increasingly considered as a potential gasification feedstock. This is mainly due not only to the expected increase in the production of waste in the coming years (which implies a need for environmentally-friendly waste management strategies), but also to the attractive and wider range of possibilities for valorisation of the waste material compared with conventional conversion routes (incineration).

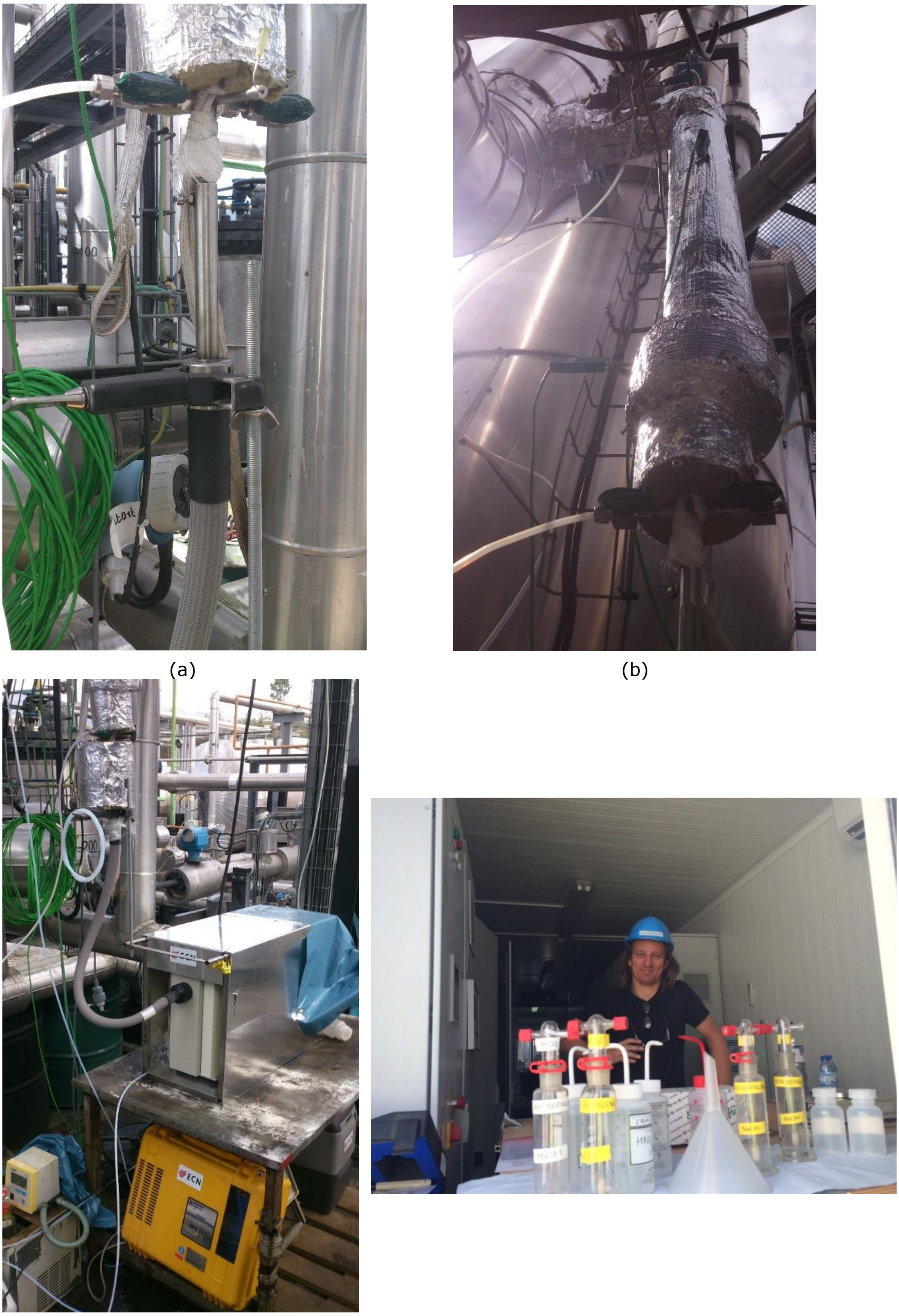
There is a wide variety of waste types, with different compositions. The inlet composition (fraction of organic matter, paper, plastics, and metals) will in turn determine the type and concentration of contaminants present in the product gas. In general, gasification of waste materials leads to higher amount of S, N. Cl and Na/K in the raw product gas. This poses challenges on the required gas cleaning train, but also poses specific requirements in the needs for gas analysis with respect to wood gasification applications in terms of target compounds and concentration levels.

An example of waste gasification process is the 4 MW_{th} Iberfer demonstration plant (Figure 68), located in Tondela (Portugal), which uses Refuse Derived Fuel as gasification feedstock [160]. The RDF is converted into product gas in a circulating fluidized bed gasifier, which is coupled to an OLGA tar removal unit [161]. The clean gas is then burned in a 1 MW_e gas engine to produced power. The plant started operation in 2009 using chicken manure as gasification feedstock, and in 2014 the plant was re-engineered and upgraded to demonstrate the use of RDF as fuel [160].

Figure 68. View of the gasification plant at Tondela (Portugal). Courtesy of Dahlman Renewable Technology.

In April 2015, ECN part of TNO performed a measurement campaign at the site, where MS equipment was tested for online analysis of tars. Figure 69 shows some pictures of the equipment and the analyses performed during the campaign. Besides micro-GC and wet chemical analysis, MS equipment was tested during this campaign [162][163]. The MS was placed after the tar removal unit to measure tar compounds online, and it was in operation for 2 days. The selected mass/charge (m/z) signals included oxygen (indication of proper gas sampling, m/z = 32), naphthalene (m/z = 128), and phenanthrene/anthracene (m/z = 178). With the selected m/z values, interference due to mass fragments was expected to be negligible. However, it is highly likely that larger molecules will form smaller fragments that can add to the selected signal, which will result in overestimation of that particular compound. Figure 70 plots the MS signals during one of the days of operation. As can be seen, the vacuum at the MS was constant during the experiment, showing no signs of clogging of the capillary sample inlet, thus indicating the proper performance of the pre-sampling system. The trends are not quantitative, since calibration was not performed.

All in all, despite short operating periods, promising results were obtained with the MS. However, this technique is suitable for relatively clean gas. It is highly likely that heavy tars cannot be measured during long periods. Since 2015, the work on MS for online tar analysis has been on hold at ECN part of TNO. Issues such as calibration for quantification, signal drift and signal interference need still to be considered.



(a) (b)

(c) (d)

Figure 69. Measurement campaign by ECN part of TNO at Tondela waste gasification plant: (a) and (b) detail of the gas sampling point (gas to MS, SPA, micro-GC and wet chemical sampling); (c) MS gas analysis equipment; (d) impingers from wet chemical analysis. Courtesy of ECN part of TNO.

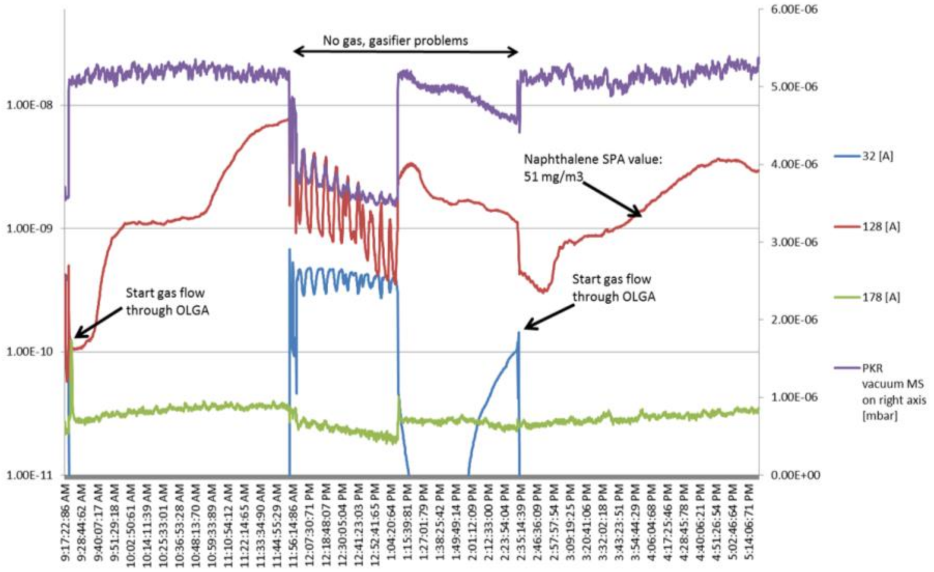


Figure 70. MS signals for online tar analysis during measurement campaign at commercial MILENA-OLGA plant operating with RDF [163]. Legend: m/z= 32 – oxygen; m/z= 128 – naphthalene; m/z= 178 – phenanthrene/anthracene; PKR: MS pressure (in mbar, right axis).

3.2.8 Gasification for liquid biofuel production - BioTfuel demonstration plant

The BioTfueL project, started in 2010, aims to develop, demonstrate and commercialize a full second-generation biomass-to-liquids process chain, schematically shown in Figure 71. The process is designed to transform via thermochemical conversion a wide range of lignocellulosic biomass (straw, forest residues, energy crops, etc.), with the possibility of co-processing solid fossil feedstock, into second generation synthetic biodiesel or biojet fuel [164][165].

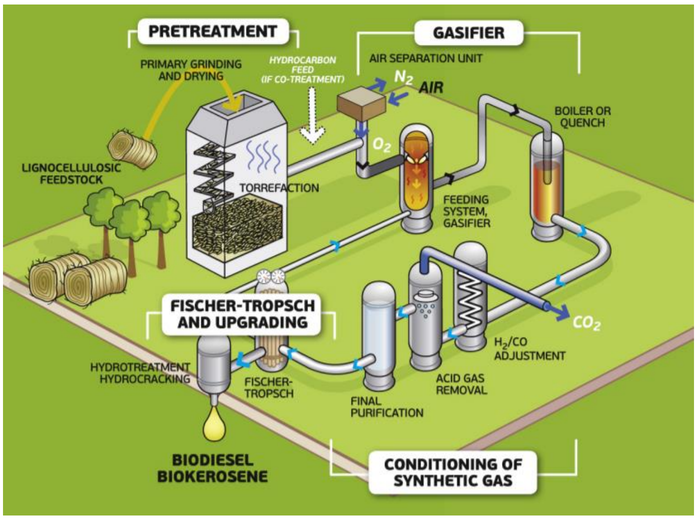


Figure 71. Schematic view of the BioTfuel thermochemical conversion route [166].

Within the framework of the project, two multi-scale demonstration plants (Figure 72) have been built providing process scale up data and validating various process schemes/configurations. The first one located in Venette (France), shown in Figure 72 (a), focuses on biomass pre-treatment with an advanced torrefaction technology designed to treat up to 5 ton/h raw biomass. The second plant, located in Dunkirk (France), Figure 72 (b), includes biomass and solid fossil feedstock preparation and gasification based on PRENFLO™ entrained-flow technology (15 MW_{th}), syngas treatment and Fischer-Tropsch test unit based on Axens Gasel-FT-technology.


(a) (b)

Figure 72. (a) BioTfueL demonstration plant at Venette (torrefaction); (b) BioTfueL demonstration plant at Dunkirk [166].

The gasification and the gas treatment sections of the BioTfuel demonstration plant at Dunkirk are instrumented with a wide variety of online gas analysers summarised in Table 22. These instruments are selected in order to adequately operate the process, measure precisely the evolution of the syngas composition and impurities along the subsequent process steps and determine the efficiency of the process chain. The whole process chain is equipped with more than 20 gas sampling systems specifically designed to ensure a good representativeness of gas samples and a fast response time for analyses.

Table 22. List of gas analysers installed in the BioTfuel demonstration plant at Dunkirk [167].

Measurement principle	Measured compounds
NDIR	CO_2, CH_4
Paramagnetic	O_2
GC-TCD	H_2, CO, N_2, CO_2, H_2O, H_2S, COS, NH_3, HCN
GC-FPD	H_2S, COS
OF-CEAS	H_2S, COS, NH_3, HCN, H_2O, CO, CO_2
AFS	Hg

3.2.9 Agricultural residue gasification for CHP production

In 2005, ECN part of TNO performed a measurement campaign at a gasification CHP plant located in Costa Rica [168]. The gasifier operated using rice husk as feedstock. During the test campaign, gas sampling was performed for measurement of tars using the tar guideline, and wet chemical analysis for the determination of NH_3 and HCN. Figure 73 shows some pictures of the campaign.

(a) (b)

(c) (d)

Figure 73. Measurement campaign at Costa Rica gasification plant: gasification plant (a); operating the gas analysis train (b); impinger train after gas sampling for tar measurement (c); impingers for wet chemical analysis after gas sampling (d). Pictures courtesy of ECN part of TNO.

3.2.10 Waste gasification for heat production – the ESKA plant

Within the ESKAGAS project, ECN part of TNO carried out in March 2018 a measurement campaign at the ESKA gasification plant located at Hoogezand (The Netherlands). The 10-13 MW_{th} circulating fluidized bed gasifier (capacity depending on the heating value of the feedstock) processes 25 kton/y of paper rejects, a waste material from the paper recycling process, similar in composition to RDF, to produce 5-16 ton/h steam for the cardboard production line, thus replacing natural gas [169]. The plant (schematic overview in Figure 74) started operation in October 2016.

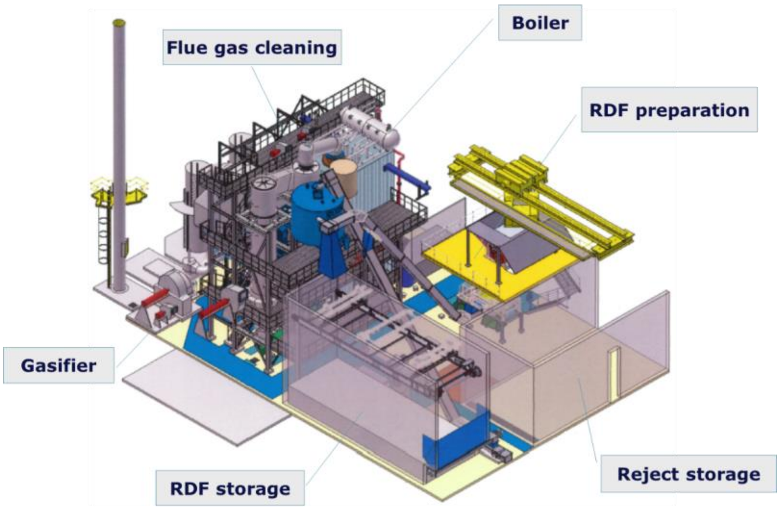


Figure 74. Schematics of the ESKA paper rejects gasification plant [169].

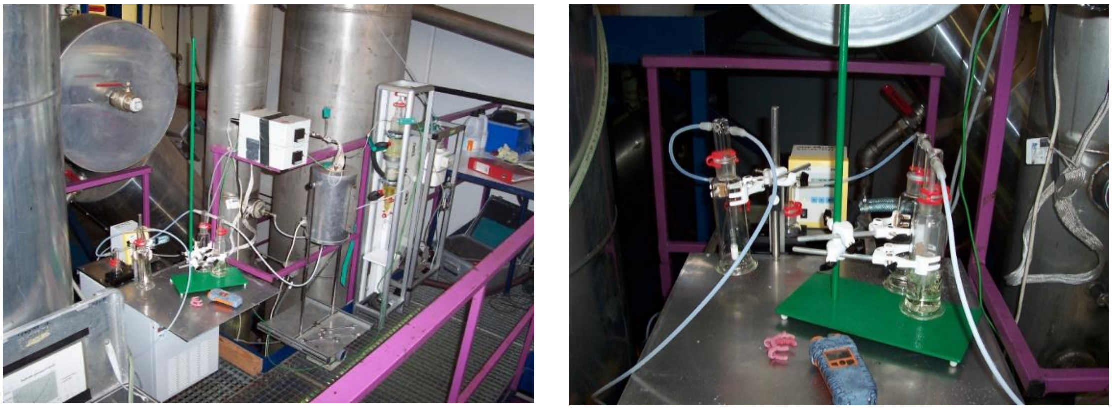
The gas was sampled at the outlet of the gasifier. The measurement campaign (Figure 75) included online gas monitors and micro-GC analysis for the measurement of gas composition, and tar guideline for the determination of tar and composition of tars (as well as the water content of the product gas). Additionally, gas bags were sampled for the offline determination of C_1-C_6 hydrocarbons (with GC-FID analysis) and sulphur compounds (with GC-FPD analysis).

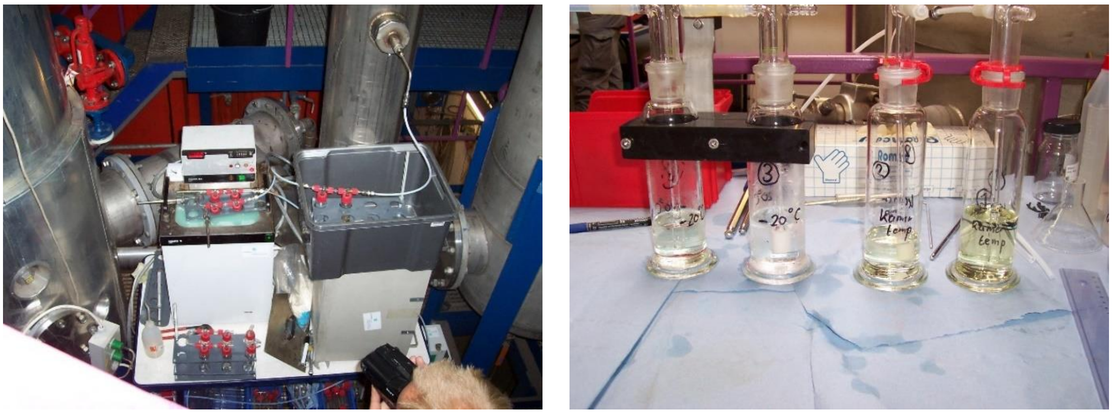

(a) (b)

Figure 75. Measurement campaign at ESKA gasification plant: (a) Gas analysis equipment; (b) Gas sampling [169].

3.2.11 Updraft gasification for CHP production – the Harboøre plant

The Harboøre plant is one of the successful references of biomass gasification. In operation since 1996, it is a 3.5 MW_{th} plant based on updraft gasification technology. 1.9 MW heat for heat district application is produced in a gas-fired boiler, whereas 1 MW electricity is generated in 2 gas engines [170][171]. In 2004, ECN part of TNO performed a measurement test at the plant for measurement of tar compounds (work within the development of the tar guideline). Figure 76 depicts the implementation of tar measurement during the campaign.


(a) (b)



(c) (d)

Figure 76. Measurement campaign at Harbøore plant (Denmark). Pictures courtesy of ECN part of TNO.

3.2.12 Gas analysis at measurement campaigns by VTT

VTT owns 2 pilot-scale gasification setups (dual fluidized bed and bubbling fluidized bed) located at the Bioruukki Pilot Centre. At each setup, there are 2 gas sampling locations – before and after the catalytic tar reformer reactor. Three different online analysis methods are applied for the measurement of light tar compounds (GC-FID), particulate material (ELPI) and ammonia (FTIR). Figure 8 shows a schematic layout of the gas analysis applied by VTT at the pilot plants.

Figure 77. Gas analysis applied by VTT at the Bioruukki Pilot Centre (left), and details of the gas dilution system (right) [19].

The main challenge for online gas analysis is the sampling of raw, tar-containing product gas. In order to overcome this difficulty, a gas dilution system based on VTT patented technology is applied [19]. The dilution system, displayed in Figure 9 and described in Section 2.2.4, can be applied to atmospheric and pressurized gasifiers. It can operate in the range of 280-800°C, and dilution ratios of 0-100 are possible with good repeatability and no problem of tar condensation in the sampling lines.

3.2.13 Gas analysis at pressurized fluidized bed gasifier at Technical University Delft

Technical University Delft has a pressurized fluidized bed pilot plant of 1.5 MW_{th} capacity (Figure 78). The bubbling fluidized bed gasifier can be pressurized up to 10 bar [79]. In the plant, gas analysis can be performed either before or after the ceramic filter for particle removal, or at different positions at the gasifier freeboard. The instrumentation available at the plant includes an FTIR analyser (for the measurement of CO, CO_2, CH_4, C_2H_4, C_2H_2, H_2O, NH_3, HCN, COS and HCl), and online gas monitors (with NDIR, NDUV and paramagnetic detectors) [79]. More information about the application of FTIR can be found in Section 2.7.2 and in Factsheet 10 in Document 2.

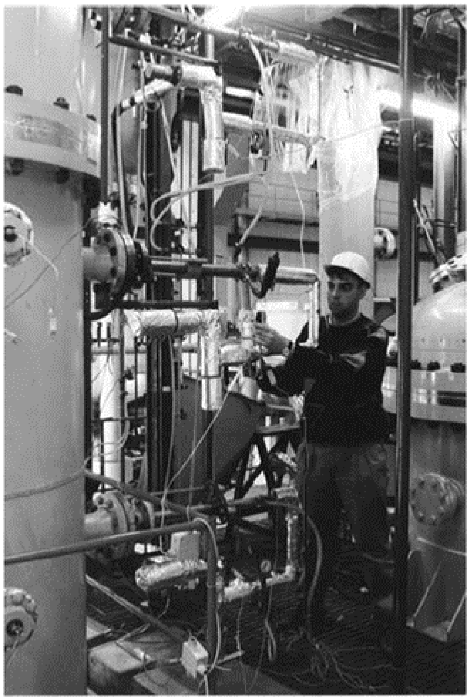


Figure 78. Pressurized fluidized bed setup at Technical University Delft [79].

3.2.14 Gas analysis at the Research Entrained flow Gasifier REGA, KIT

REGA is a bench-scale (60 kW_{th}) atmospheric entrained-flow gasifier located at KIT laboratories (Germany). Research work focuses on the detailed understanding and description of the sub-processes taking place during entrained flow gasification of suspension fuels. Figure 79 shows the process flow scheme. A maximum of 13 kg/h liquid and suspension fuels are gasified using oxygen-enriched air as gasification/atomization medium. The heat loss of the reactor is minimized by electric heating of the reactor walls. Operating parameters like stoichiometry, process temperature and atomization can be varied independently.

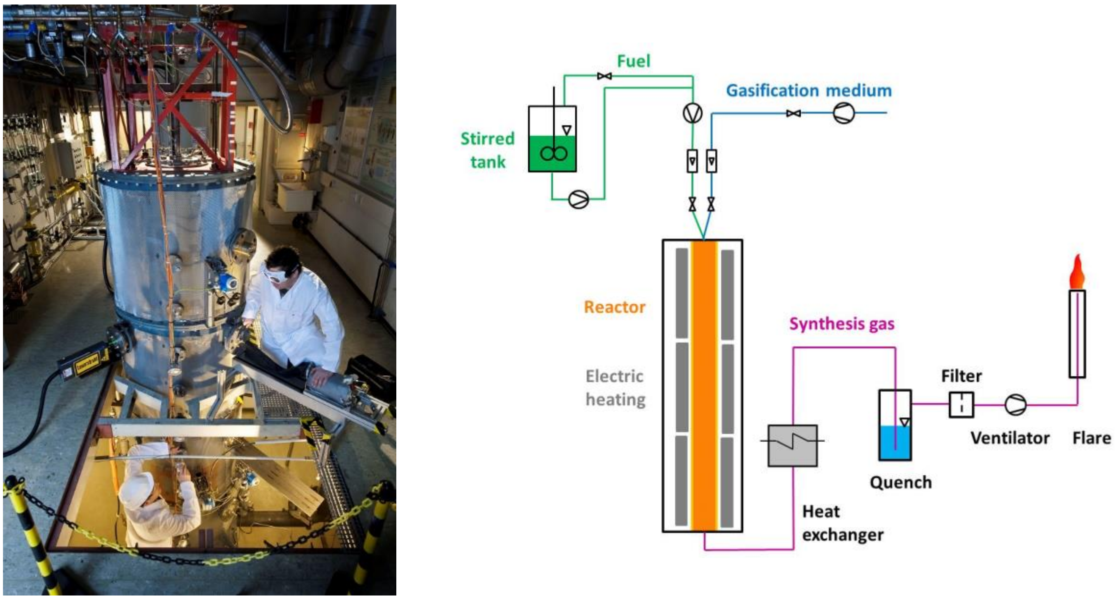


Figure 79. Picture and process flow scheme of the REGA bench-scale gasifier [159].

The reactor is equipped with flanges along the reactor axis for sampling probes and thermocouples access. For laser-based measurements the flanges can be equipped with optical access glasses which are purged with nitrogen. The burner is mounted at the top of the reactor. By means of a vertically movable burner construction the burner position can be shifted in axial direction. Thus, measurements can be taken at any distance from the atomizer, enabling complete data mapping of the reactor. Fuel conversion is determined by measurement of the gas phase composition at the reactor outlet.

Figure 80 shows the setup of the gas sampling system applied at REGA. Gas samples are extracted from the reactor using cooled steel probes with a ceramic tip. The samples are quenched by thermal oil at 80°C to prevent further reactions in the sampling line. After passing a filter, a part is cooled to 3°C, the dry samples are then analysed using standard gas phase analysers or micro-GC. Organic carbon is measured in the wet gas using a Flame Ionization Detector operated at 160°C. Table 23 lists the measurement principles and accuracies of the standard gas phase analysers used at the setup.

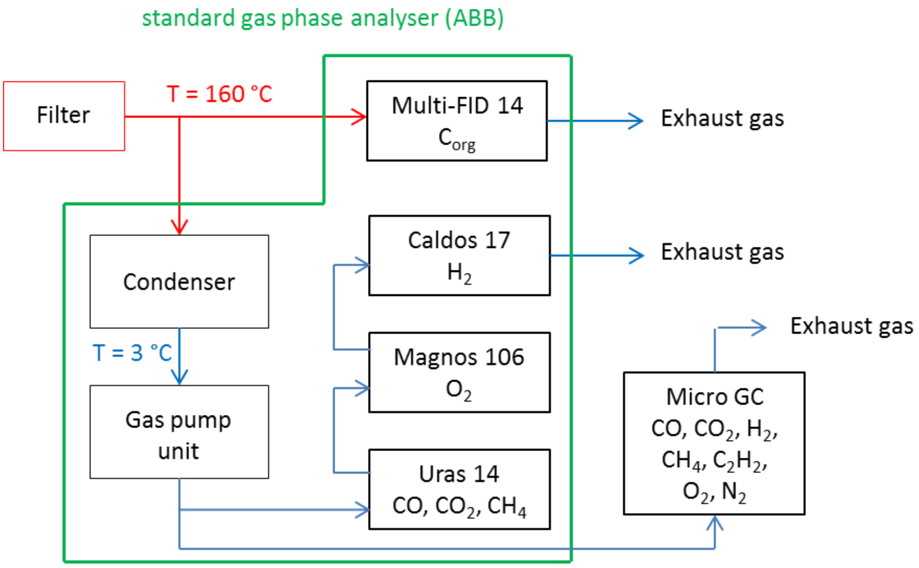


Figure 80. Setup of gas sampling system used at the REGA setup [159].

Table 23. Overview of features of gas measurements applied at the REGA setup.

Species	Principle	Measurement range	Accuracy of reference gas (vol.%)	Accuracy of analyser signal
H_2	Thermal conductivity	0–50 vol.%	±0.39 vol.%	±0.25 vol.%
CO	NDIR	0–50 vol.%	±0.46 vol.%	±0.10 vol.%
CO_2	NDIR	0–30 vol.%	±0.44 vol.%	±0.06 vol.%
CH_4	NDIR	0–10 vol.%	±0.002 vol.%	±0.02 vol.%
O_2	Paramagnetic	0–15 vol.%	-	±0.08 vol.%
Organic C	FID	0–10 g/m^3	-	±50 mg/m^3

The micro-GC unit (Figure 81) has 4 channels, each of them equipped with individual analytical modules. In Table 24 the configuration of the channels with the different columns and the calibrated species are listed. Channel 4, for the measurement of BTX, is currently not calibrated. The gas phase concentrations are determined with TCD detectors.

Table 24. Columns and species detected by micro-GC used at REGA setup.

	Channel 1	Channel 2	Channel 3	Channel 4
Column	Molecular sieve (pore diameter 0.5 nm)	Non-polar capillary	PoraPlot Q capillary	Non-polar polydimethyl-siloxane
Species / Measurement range	H_2: 0 – 30 vol.% O_2: 0 – 21 vol.% N_2: 0 – 100 vol.% CH_4: 0 – 2 vol.% CO: 0 – 30 vol.%	C_2H_6: 0 – 1 vol.% C_2H_4: 0 – 1 vol.% C_3H_8: 0 – 0,5 vol.% C_3H_6: 0 – 0.5 vol.% C_2H_2: 0 – 1 vol.%	CO_2: 0 – 25 vol.% C_2H_2: 0 – 1 vol.% C_3H_8: 0 – 0.5 vol.% C_3H_6: 0 – 0.5 vol.% H_2O: 0 – 5 vol.%	BTX

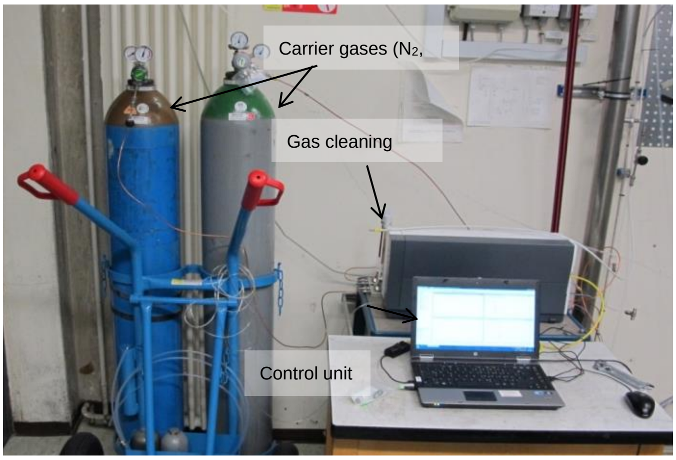
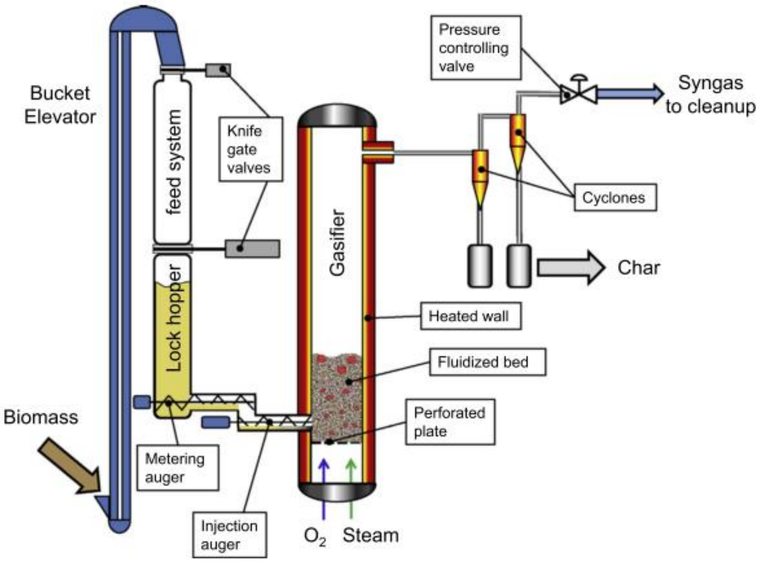


Figure 81. Micro-GC analyser at REGA setup [159].

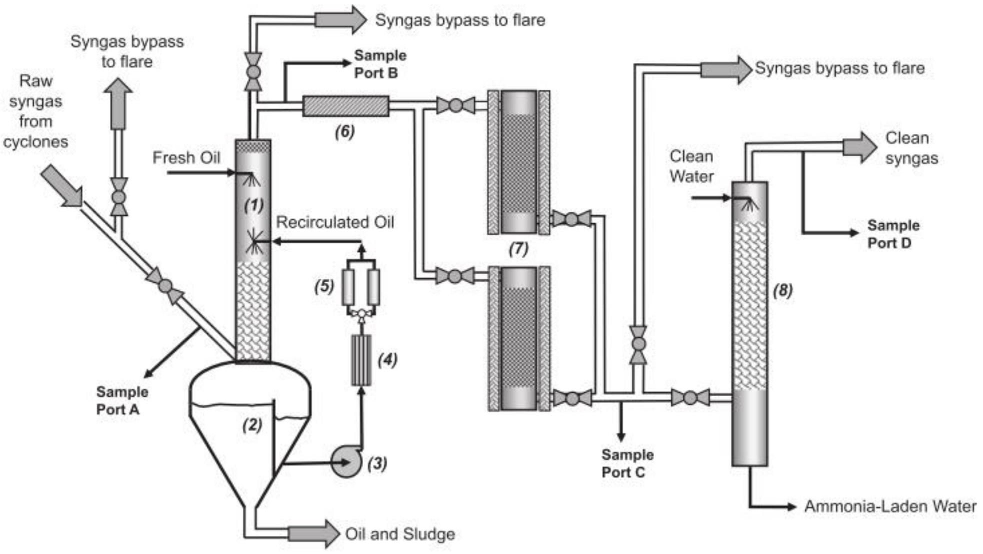
Besides extractive measurements, laser based measurements have been carried out by the cooperation partner German Aerospace Centre applying TDLAS, LII and LIBS [18]. Further details about the implementation of TDLAS in the REGA gasifier can be found in Section 2.8.4.

3.2.15 Gas analysis at Iowa State University

The Bioeconomy Institute at Iowa State University is one of the most active research players in the field of biomass gasification and biofuel production in the United States. The gasification plant at Iowa State (Figure 84) consists of a 25 kg/h oxygen/steam fluidized-bed gasifier with a cleaning system to produce Fisher-Tropsch ready syngas. The schematic of the feed system, gasifier and cyclones are displayed in Figure 82 (a). The gas cleaning consists of (1) oil scrubbing column for removing fine char and tars, (2) oil decanter tank for allowing collected solids to settle out of oil, (3) oil circulation pump, (4) oil cooling heat exchanger, (5) oil filter, (6) electrical syngas circulation heater, (7) packed bed sulphur adsorbent canisters, and (8) water scrubber for ammonia removal. The gas cleaning system that was integrated with the gasifier, consists of column and scrubbers to remove tar, sulphur, and ammonia is displayed in Figure 82 (b). The complete gasifier system is displayed in Figure 83. The gas compounds are measured online with the GC-NCD/SCD/TCD/TCD (Figure 21) to monitor cleaning efficiencies at the various stages of syngas cleaning, utilizing the online ports that are outlined in Figure 84.



(a)



(b)

Figure 82. Iowa State University's 25kg/h fluidized bed gasifier (a) and gas cleaning system (b) [22].

Figure 83. The complete Iowa State University 25 kg/h gasifier and cleaning system [172].

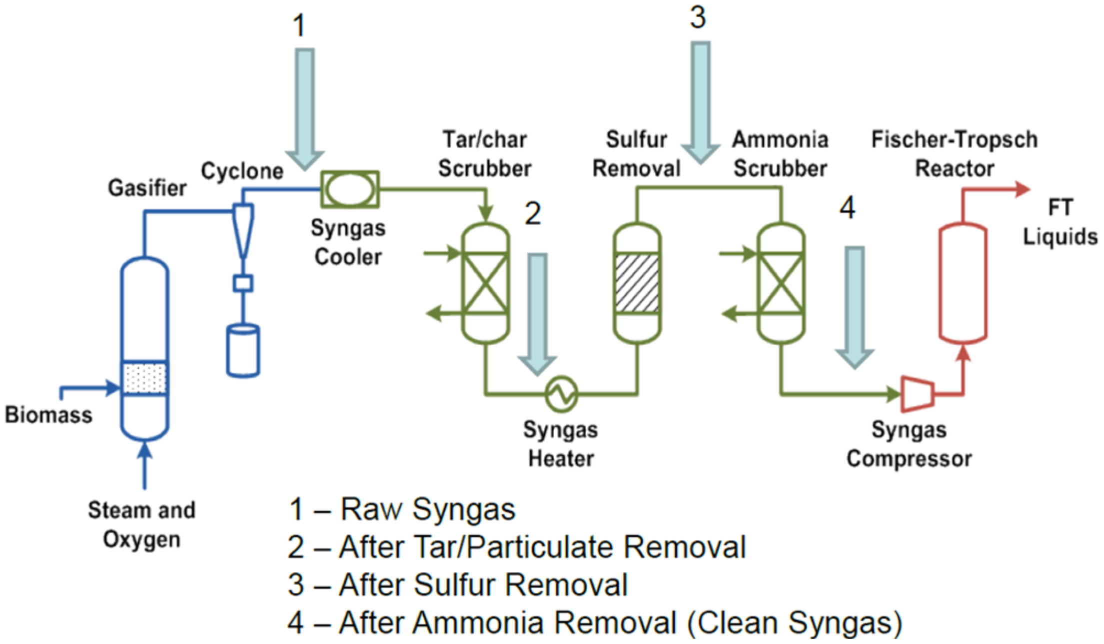


Figure 84. Schematic of the biomass gasification to biofuel located at Iowa State University [76][172].

The biomass gasification setup at Iowa State owns a unique, custom-built GC instrument which allows the online analysis of a large number of gas compounds. The GC unit (shown in Figure 21, Section 2.5.2) has 11 columns and 5 detectors [76]:

- Dual Thermal Conductivity Detectors (TCD): CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, H_2, CO_2, N_2, CO , NH_3 (detection limit: 500 ppmv).

- Sulphur chemiluminescence detector (SCD)- Dual plasma system:

    - Hydrogen sulphide (range 10 ppbv – 1000 ppmv).
    - Carbonyl sulphide, carbon disulphide, sulphur dioxide (lower detection limit: 10 ppbv).
    - Mercaptans (lower detection limit: 10 ppbv).

- Nitrogen chemiluminescence detector (NCD): ammonia, hydrogen cyanide, nitric oxide (lower detection limit: 100 ppbv).

- Electron capture detector (ECD): nitrous oxide (lower detection limit = 100 ppbv, not applied in gasification).

Moreover, Iowa State University has good experience in wet chemical analysis for the offline measurement of NH_3 and HCN [88][109]. More details about the setup for the sampling of tar, NH_3 and HCN can be found in Sections 2.5.2 (tar) and 2.7.2 (N compounds).

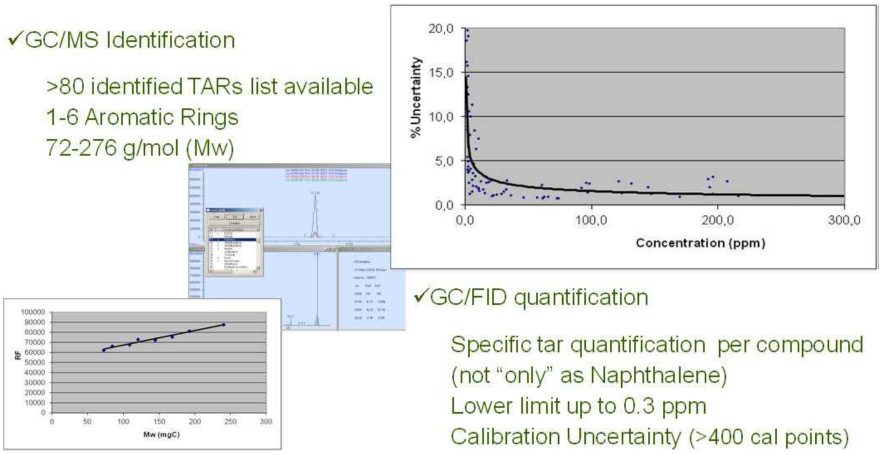
3.2.16 Small-scale gasification for combined heat and power (CHP) – GaST project

Within the GaST project, Free University of Bolzano (UNIBZ) performed a screening of the performance of a number of small-scale CHP plants. For the comparison, the mass and energy flows of the CHP plant (gasifier and gas engine) were measured for 5-6 hours. For the quantification of the heating value of the product gas, the gas composition was measured using micro-GC analysis, whereas the tar guideline (CEN/TS 15439) was applied for the quantification of tars [173][174][175][176]. Figure 85 shows some pictures from the measurement campaigns performed. Factsheet 41 on tar guideline in Document 2 contains more details about the configuration of the impingers train during this project.

Figure 85. Gas analysis at measurement campaign by RE-CORD and UNIBZ in small-scale gasification plants [175][176].

3.2.17 Gas analysis at CENER gasification pilot plant

Figure 87 illustrates the implementation of particles and tar analysis by CENER at their 2 MW_{th} gasification pilot plant. The whole equipment assembling process, sampling and sample preparation for transportation to the laboratory analysis requires 2 hours per sample (in-house measurements) or 4 hours (sampling at external sites). Gas sampling from the gasifier usually takes typically between 30 and 60 minutes. Whereas particulate matter is gravimetrically determined after Sohxlet extraction (lower detection limit 20 mg/Nm^3), tars are measured at the laboratory by gas chromatographic techniques: GC-MS for identification and GC-FID for quantification (Figure 86). In the case of GC-FID quantification, CENER has developed a calibration procedure based on the determination of response factors depending on tar carbon content and the number of aromatic rings for each tar compound, which allows low uncertainty levels (up to 0.3 ppmv).



✓GC/MS Identification

>80 identified TARs list available
1-6 Aromatic Rings
72-276 g/mol (Mw)

✓GC/FID quantification

Specific tar quantification per compound
(not “only” as Naphthalene)
Lower limit up to 0.3 ppm
Calibration Uncertainty (>400 cal points)

Figure 86. GC-MS and GC-FID applied at CENER: calibration procedure developed by CENER for quantification of tars.

In the case of gas analysis during the measurement campaigns, the gas composition (H_2, CO, CO_2, N_2, O_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, and C_6H_{14}) is measured in dry basis. The gas concentration is online measured using micro-GC (GC-TCD) according to CENER's internal procedure. The product gas is continuously sampled with a heated probed and conditioned prior to analysis in order to avoid shutdown. Particles are retained in the body of the heated probe by an exchangeable filter, and the raw gas (including water and tar) is conducted to a rack by a heated transfer line. Both the probe and the transfer line temperature are heated above the tar dew point (up to 200-225ºC). The gas entering the rack is firstly cooled down below 5ºC in 2 cooling steps, and after that passed through a coalescence filter and a silica gel filter in order to remove water and tars.

Figure 87. Gas sampling during measurement campaign at CENER (left) and implementation of tar guideline sampling [177].

3.2.18 Gas analysis at BFB pilot plant at University of Seville

The Bioenergy research group of University of Seville (Spain) operates a 150 kW_{th} bubbling fluidized gasifier pilot plant (Figure 88). The gasifier can operate with air, steam, oxygen and mixtures thereof as gasifying agent. A wide range of biomass and waste feedstock (wood, olive bagasse, sewage sludge, meat and bone meal, MSW, etc.) have been tested in this pilot scale [178].

Figure 88. View of the 100 kW_{th} BFB pilot plant located at University of Seville [85].

The sampling line for gas analysis used in this pilot plant is schematically depicted in Figure 89. A common gas sampling probe (designed according to the specifications of the CEN/TS 15439 for tar/particle sampling) takes gas to 2 lines. One of them is used for the application of the tar guideline, whereas the second line is used for wet chemical sampling for the determination of H_2S, HCN, NH_3 and HCl [85]. A Pitot tube is implemented for the determination of the gas velocity (required for the isokinetic sampling and measurement of particulate matter).

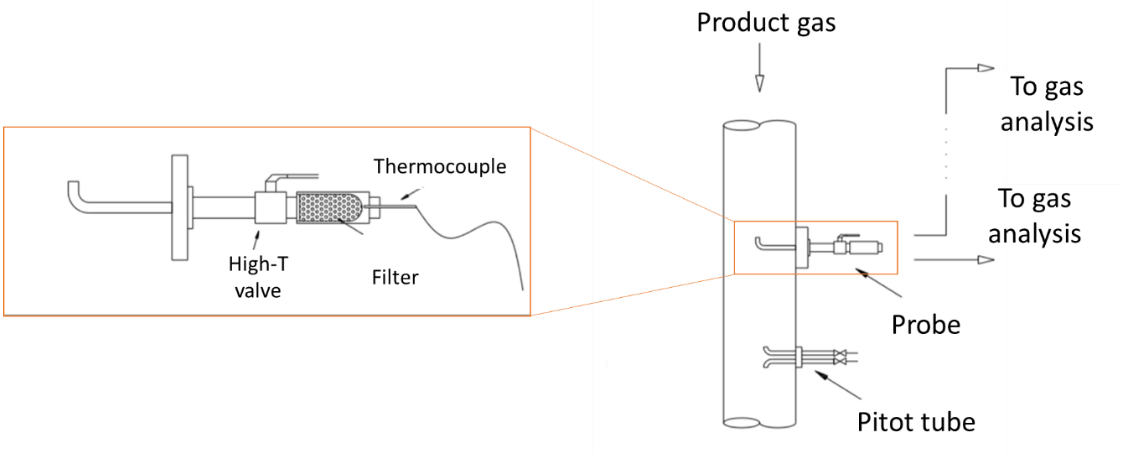


Figure 89. Schematic layout of gas sampling at BFB pilot plant at University of Seville [85].

3.2.19 Gas analysis at the 2-4 MW Chalmers indirect gasification pilot plant

The Chalmers pilot plant consists of 2-4 MW_{th} indirect gasification section which is integrated with the loop of an 8-12 MW_{th} circulating fluidized bed boiler [139][179]. This pilot plant has been extensively used for the investigation of the gasification performance of a wide range of gasification feedstock under different operating conditions. In this section we briefly describe some examples of measurement campaigns carried out at the Chalmers pilot plant focused on measurement of particles and aerosols contained in the product gas.

A semi-online particle measurement system (Figure 90) developed by Linnaeus University for sampling aerosol particles in hot product gas from fluidized bed gasification was tested at Chalmers [180]. To reduce coagulation and nucleation of the particles, a dilution probe was used to sample the hot product gas and dilute it with heated nitrogen (approximately 770°C) at the probe tip. In the probe the diluted gas temperature was reduced to about 300°C, thus above the dew point of tar components. Downstream the dilution probe, the aerosol entered the primary thermodenuder (TD), which is divided into a heating and an adsorber section. The temperature of the heating section was set to 300°C. The adsorber section consists of inner and outer replaceable activated carbon cartridges where evaporated tar compounds are adsorbed to prevent condensation and the formation of particulate matter as the sample gas was further cooled. The aerosol exited the adsorber section at a temperature of about 30°C.

To extract a certain flow of diluted product gas from the probe and to produce an additional dilution, an ejector diluter was used downstream of the primary thermodenuder. An oven-heated reactor was connected downstream the ejector, which could be bypassed. The reactor can behave like a secondary thermodenuder for further tar removal, and can also heat up the aerosol again at different temperatures to investigate both thermal stability and reactivity of particles [181][182][183]. It can be used as whether any condensation from tar or inorganic vapours occurred. Downstream the aerosol extraction system, a number of analysis instruments (APS, SMPS, ELPI, TEOM and LPI) are applied for the characterization of the aerosols. All the instruments are connected downstream the oven reactor. A gas analyser is additionally used to measure the CO concentration after dilution in order to estimate the total dilution ratio by comparison with CO concentration measured in the raw product gas.

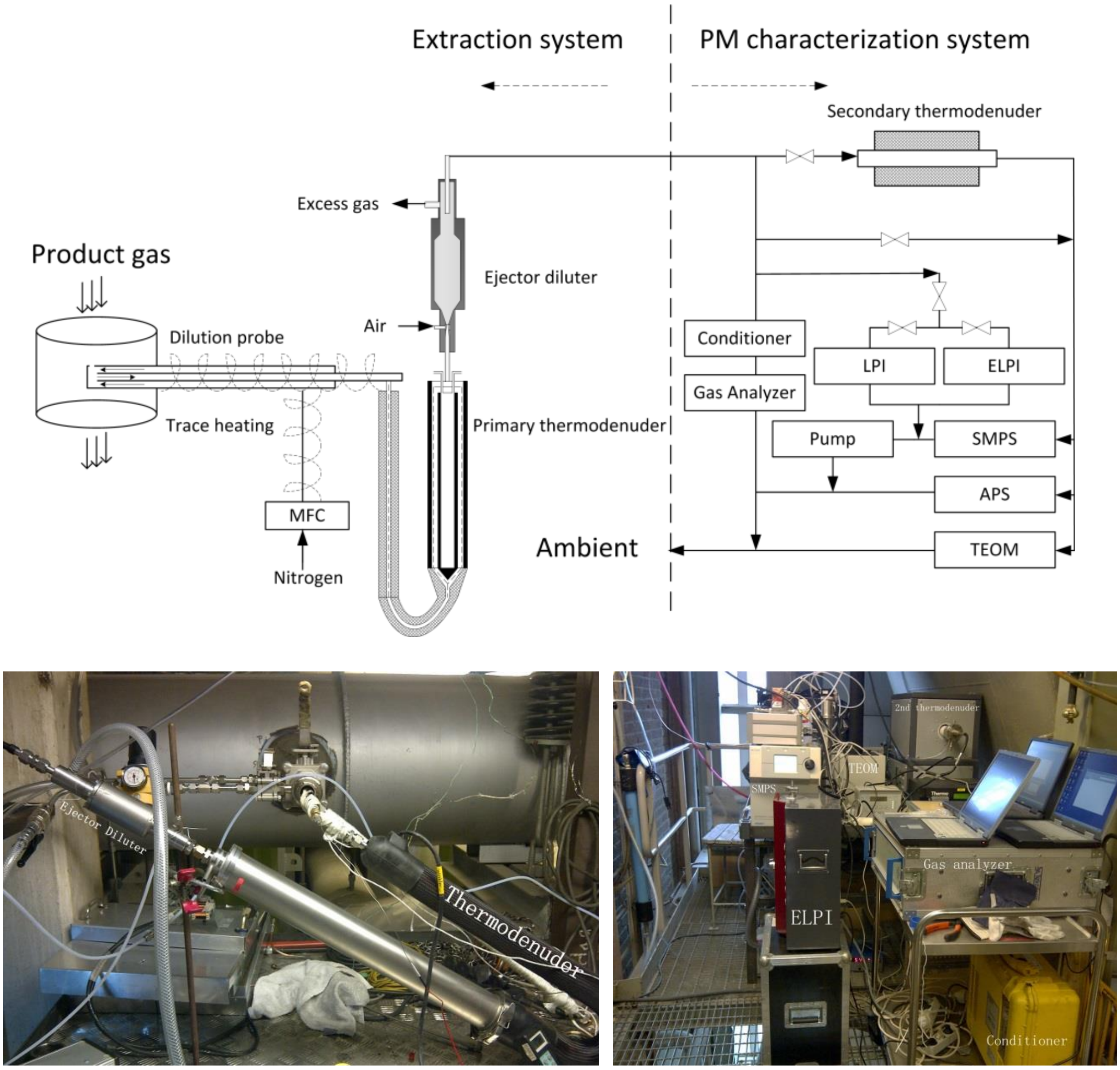
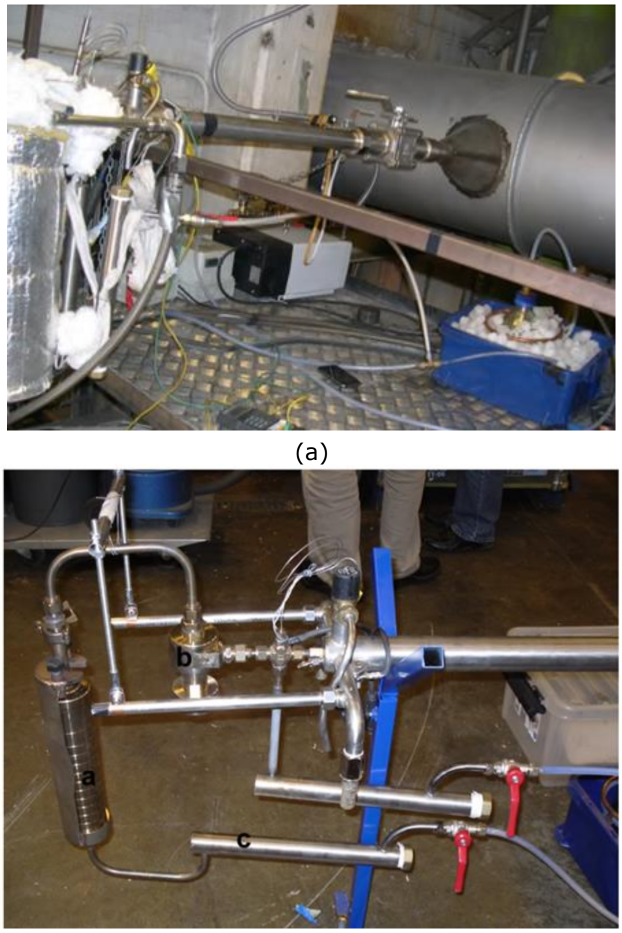


Figure 90. Aerosol particle measurement system at Linnaeus University: schematic layout (top), and implementation during measurement campaigns in the 2-4 MW Chalmers indirect gasifier [180].

The aerosol measurement system developed by Linnaeus University has been applied at different biomass gasification pilots and plants: the 100 kW steam-O_2 blown CFB at Delft University of Technology [143], the 2-4 MW Indirect BFB at Chalmers Technical University [180][184], the 20 kW BFB gasifier at TPS Termiska Processer AB [185], and the 500 kW Woodroll gasification pilot plant by Cortus Energy. In Figure 90 it can be observed as an example the implementation of the aerosol measurement system at the Chalmers pilot plant.



(a)

(b)

Figure 91. Particulate matter sampling at the Chalmers gasifier pilot plant by SGC [139]: (a) gas sampling probe and particle separation unit; (b) particle separation unit: a – low-pressure impactor (LPI); b – cyclone; c- heat exchanger.

Hermansson et al. [139] from the Swedish Gas Technology centre (SGC) describe a measurement campaign for sampling of particulate matter at the Chalmers gasifier. A high-temperature probe was used for particle sampling, together with a particle separation system composed of a cyclone and a low-pressure particle impactor. The particles collected were analysed in terms of mass and particle size distribution. The particle sampling was performed downstream the gasifier using a heated isokinetic sampling probe (Figure 91), where the gas was rapidly cooled to 350°C. The particle sampling device was thermally heated and insulated to avoid cold spots where condensation of tars and/or water can take place. A high-temperature particle separation unit (Figure 91 (b)) was installed. Two configurations of particle separation were tested: a single 13-stage low-pressure impactor (LPI), and a cyclone (10 mm) + LPI combination. The whole system was heated at 350°C. The operating high temperature put stringent requirements on the materials of the setup. The separated gas was cleaned from tars before being released to the atmosphere. The gas flow rate, determined as 6.4 NL/min, was calculated from the pressure drop and the impactor temperature (calibration data of the impactor). After gas sampling, the collected particles were further offline analysed: gravimetric determination of the particle content, particle size distribution, and chemical analysis via X-ray diffraction (XRF). The results indicated that placing a cyclone upstream the impactor was crucial to avoid disturbance of the sampling of the particles below 5 μm by removing the bulk of inert particles derived from the fluidized bed gasification process. Without the cyclone, there is an extensive load of particles in the collection plates of the LPI due to the presence of large bed material particles, which bounce and scatter inside the impactor, leading to a loss of particles and thus to uncertainty in the total amount of particles and particle size distribution [139].

3.2.20 Gas analysis at the Cortus Energy pilot plant

Cortus Energy has developed the WoodRoll gasification technology, in which pyrolysis and gasification are physically separated in different stages [186]. As part of the commercialization development, Cortus Energy erected a 500 kW_{th} pilot plant located at Köping (Sweden). The gasifier has a capacity of 200 kg/h wet biomass (equivalent to 50 kg/h charcoal used as fuel for the steam gasification stage). The resulting syngas produces 500 kW thermal power. The plant operates in a 3-shift continuous process, 5 days per week [187].

An example of measurement campaign is reported by Amovic et al. from the Swedish Gas Technology Centre (SFC) [187]. In order to perform mass and energy balances to the process, analysis of solids (biomass fuel and ash), liquids (tars and water condensate), and gas were carried out. Product gas composition (Ar, H_2, N_2, O_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_2H_2) was online measured using micro-GC analysis, whereas gas monitors were used for in-situ exhaust gas analysis. Before entering the analysis system, the gas (2.5 L/min) needs to be conditioned to remove particles, tars, water, ammonia and H_2S. This is done in a train of washing bottles filled with water or 2-propanol, a cooler, a filter and a pump.

The composition of the tar from the gasification stage was determined using SPA analysis (samples being externally analysed). However, SPA was not suitable for the analysis of the tar compounds from the pyrolysis stage. In this case, gas was sampled through a gas cleaning line, and tars and water were collected in gas washing bottles. Since the exact chemical composition of the pyrolysis tars was claimed to be nearly impossible, just gravimetric determination, energy density and ultimate analysis (C, H, O) was applied to the pyrolysis tar. The water content in the gas was gravimetrically determined, and offline, external chemical analysis was performed. Gas bags were also taken, and were externally, offline analysed for the determination of the content of NH_3, H_2S and HCN [187].

3.2.21 Gas analysis at the Swedish Gasification Centre (SFC)

The Swedish Centre for Biomass Gasification (SFC) is a 10-year research program started in 2011, which was created to coordinate and support established Swedish research in the area of biomass gasification. The Centre consists of 3 independent research nodes that focus on different gasification technologies: direct fluidized bed gasification (CDGB node, led by KTH), indirect fluidized bed gasification (CIBG node, led by Chalmers Technical University), and suspension gasification (Bio4G node, led by Luleå Technical University).

Within SFC, robust measurement methodologies and analytical techniques have been developed for the closure of mass and energy balances in industrial gasification processes [188]. This good precision can largely be attributed to the development of a high-temperature reactor (HTR) within the CIGB node that is operated at 1700°C and fed with a slipstream of raw gas from the Chalmers gasifier [189]. These conditions permit decomposition of the gas species to a stream consisting of H_2, CO and CO_2. Thanks to this technique, SFC has been able to close the mass balance of a gasification system that operates at low temperatures (typically below 850°C), while validating measurements of individual tar species down to benzene using solid-phase adsorption (SPA) combined with active coal. Moreover, extensive work on measurement techniques has been conducted by RISE (Research Institutes of Sweden) and the University of Gothenburg, principally for the online quantification of alkali, tars, and particulates [126][127][190][191]. This development was conducted in close collaboration with Chalmers University of Technology and tested in the Chalmers gasifier and in full-scale operation in the GoBiGas facility. Further information about the high-temperature reactor developed by Chalmers can be found in Section 4.4.

SFC researchers working the Bio4G node have developed a diode-laser-based system for highly sensitive extinction measurements of low soot concentrations. The system, which facilitates high temporal resolution and automatic background subtraction, was initially tested and used for detailed flame studies of soot formation and for evaluation of soot optical properties in lab-scale flames [192]. The diode system was successfully applied in a dual-wavelength approach in an atmospheric air-blown entrained-flow gasifier at RISE [193]. Measurements were run at various equivalence ratios, for two fuels (wood and peat), and for two burner configurations (swirl and jet).

The laser-induced incandescence (LII) and elastic light-scattering (ELS) techniques were developed and combined for simultaneous soot volume fraction and particle size measurements. This combined technique was used to study the influence of metals on soot-formation processes at concentrations corresponding to those present in entrained-flow gasifiers [192]. The results indicate that alkali metals, especially potassium, had a large impact on the soot-formation processes: alkali metals are expected to contribute to lower soot concentrations and smaller particles in entrained-flow gasifiers.

Additionally, SFC researchers have developed three IR TDLAS sensors for measurement of concentrations of major species of product gas (CO, H_2O, and CO_2), temperature, and soot volume fraction under gasification/combustion conditions [194]. The sensors were tested in flat flames; comparison of the measured concentrations with the results of 1-D modelling indicates very good agreement, generally better than 10%. The accuracy of temperature measurements was evaluated by comparing the temperatures measured in near-adiabatic flat flames with calculated adiabatic values. Application of the TDL sensors for simultaneous real-time detection at different locations in the reactor core of a pilot-scale biomass gasifier operating in gasification and combustion modes was demonstrated. From these measurements, the density-weighted, path-averaged temperature and CO, CO_2, H_2O, and soot concentrations were derived and conclusions concerning the progress of the gasification reactions were made. The TDLAS sensors performed well under harsh, high-temperature conditions and in the presence of high soot concentrations. The advantages of these new types of laser-based sensors over conventional diagnostic equipment were also demonstrated [195].

TDLAS sensors for H_2O, gas temperature, and potassium have also been developed by Umeå University for real-time in situ diagnostics in biomass gasification processes (Figure 92). The first sensor measures path-averaged concentrations of H_2O and H_2O-density-weighted, path-averaged gas temperature [196][197]. The second sensor can quantify the concentration of atomic potassium in flames and hot-reacting flows over a wide dynamic range [198]. Both instruments can also measure soot volume fractions and have been combined to detect all four parameters simultaneously in the same sample volume.


(a) (b)

Figure 92. TDLAS system developed at Umeå University: (a) view of gasifier (100 kW_{th} at Piteå) with TDLAS implemented; (b) portable, fibre-coupled optical setup in control room. Pictures courtesy of Umeå University.

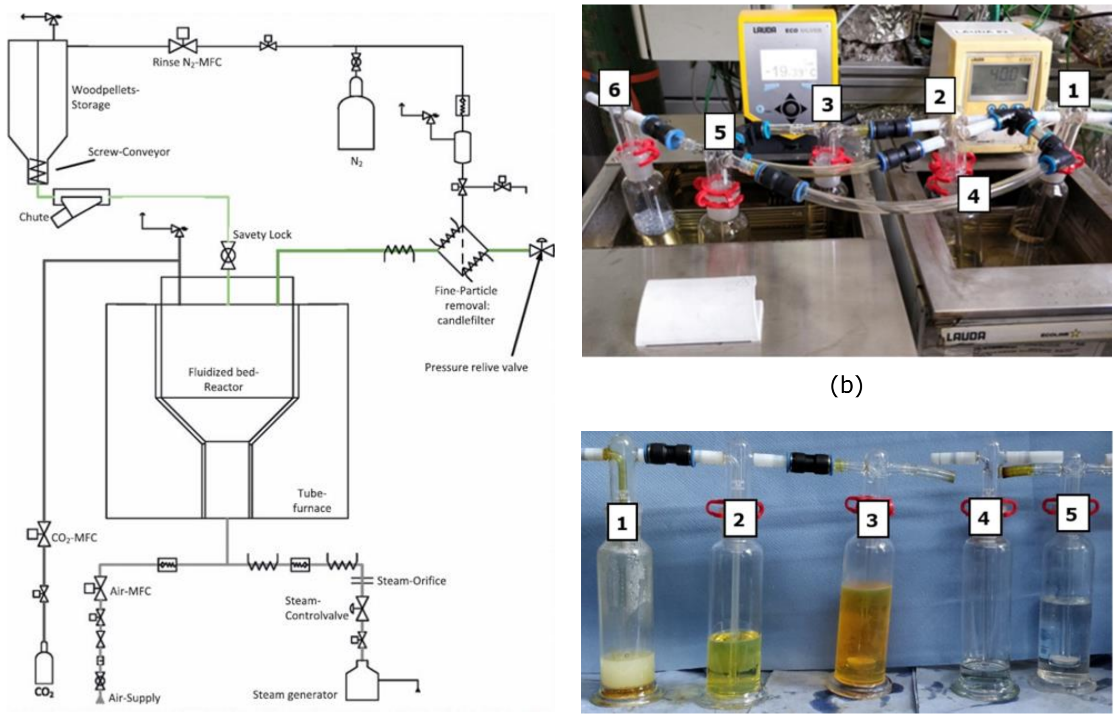
The setups described above have been extensively validated in flat flame burners and laboratory furnaces [196][197][198][200]. Moreover, these robust and portable sensors have been used for measurements near single biomass pellets during thermochemical conversion [196], in the reactor core of a research-scale entrained-flow reactor (EFR) at Umeå University [197], and in the reactor core of a pilot-scale EFR at RISE ETC during biomass gasification [195] and combustion. Under practical conditions, measurements of gas temperatures can be performed at least in the range of 1200–1800 K with 50 K accuracy; water content can be measured down to around 0.1%; and atomic potassium can be detected in a six-orders-of-magnitude dynamic range from 40 pptv·cm to 40 ppmv·cm. The measurement time resolution is typically 0.01 s. The sensors work well even at high soot concentrations (up to 99% light extinction due to soot).

In the experimental campaigns, it was demonstrated that the TDLAS sensors can monitor the progress of biomass conversion in the reaction zone of entrained-flow reactors, and that the measured parameters represent well the conditions that the fuel particles experience in the different conversion steps. Rapid changes in process parameters have been observed and attributed to fuel feeding fluctuations [195]. Measured water content and gas temperature agree well with 2D numerical simulations, and the atomic potassium concentrations at the end of the process are in excellent agreement with thermodynamic equilibrium calculations [199]. In conclusion, the TDLAS sensors are well suited for both fundamental laboratory studies and application in research- and pilot-scale entrained-flow reactors.

Within the CDBG node managed by KTH, work has continued in improving the SPA procedure in terms of the accuracy and the practicalities of sampling, extraction and analysis. In addition, work to develop a similar method for BTX is ongoing. Optical methods for total tar measurement and alkali measurement are also under development [188].

3.2.22 Gas analysis at Technical University Graz

The bubbling fluidized-bed gasifier available at the laboratories of TU Graz (approximately 1.5 kW using wood pellets) can be used to test different gasification operating conditions and different pelletized feedstocks. The great stability achieved in the gasifier allows performing stable long-term tests in which investigations for gas cleaning and utilization can be conducted with real product gas during several days. This gas is used to examine catalytic tar cracking, methanation, desulfurization, hydrodesulfurization or coupling with fuel cells.



(b)

(a)

(c)

Figure 93. (a) Schematic view of the TU Graz gasifier; (b) Tar sampling; (c) Impingers after tar sampling. Pictures courtesy of TU Graz.

Biomass is gasified at temperatures of 700°C to 800°C under allothermal conditions with steam as fluidization medium. Mixtures of steam and air can be also used as a fluidization agent. The reactor pressure can be increased up to 5 bar. The heat for the allothermal operation is supplied by an electric tube furnace with a capacity of 4 kW. A steam generator injects superheated steam at 400°C through a nozzle at the bottom of the reactor, ensuring a good mixing and stable fluidization conditions. Fuel is supplied from a storage tank through a charging screw to the inlet at the top of the reactor. Olivine is commonly used as the bed material. After the gas leaves the reactor, the particle matter of the product gas is removed in a metallic filter candle. The filter and all piping are heated to a temperature of 350°C to prevent the condensation of tars. A schematic view of the gasifier can be seen in Figure 93 a).

The setup for measuring tars follows the tar guideline and includes 5 impinger bottles filled with 100 mL isopropanol at temperatures of +40°C (Bottles 1, 2 and 4) or -20°C (Bottles 3 and 5), and a safety bottle filled with glass beads (bottle 6) to capture evaporated isopropanol at -20°C. The tar sampling setup with impinger bottles at -20°C and +40°C is shown in Figure 93 (b). The impinger bottles after 40 minutes of measurement time with a flow rate of approximately 0.3 Nm^3/h are shown in Figure 93 (c). The gasifier was operated with steam at a temperature of 750°C and with wood pellets as feedstock. The obtained gravimetric tar content is in the order of 10 g/Nm^3 with these conditions. The first bottle captures most of the water in the product gas and an emulsion is formed. The second and third bottle contain a significant amount of tars, while the isopropanol in bottle 5 is nearly transparent, which is a good indicator that most of the tar compounds are captured with this system. Some of the isopropanol in the bottles at +40 °C is evaporated and condensed in the bottles at -20°C, which is the reason for the different liquid level in the bottles. During the measurement time, the permanent gas components are monitored by a gas monitor which quantifies O_2, CO, CO_2, CH_4, and H_2, or via a GC-TCD, whereas sulphur compounds in the gas phase can be measured by GC-PFPD. The gathered liquid sample is then used for the gravimetric determination of tars with a rotary evaporator and can also be examined with GC-FID to measure the tar components or GC-PFPD to measure organic sulphur compounds.

3.2.23 Gas analysis at CEA pilot plants

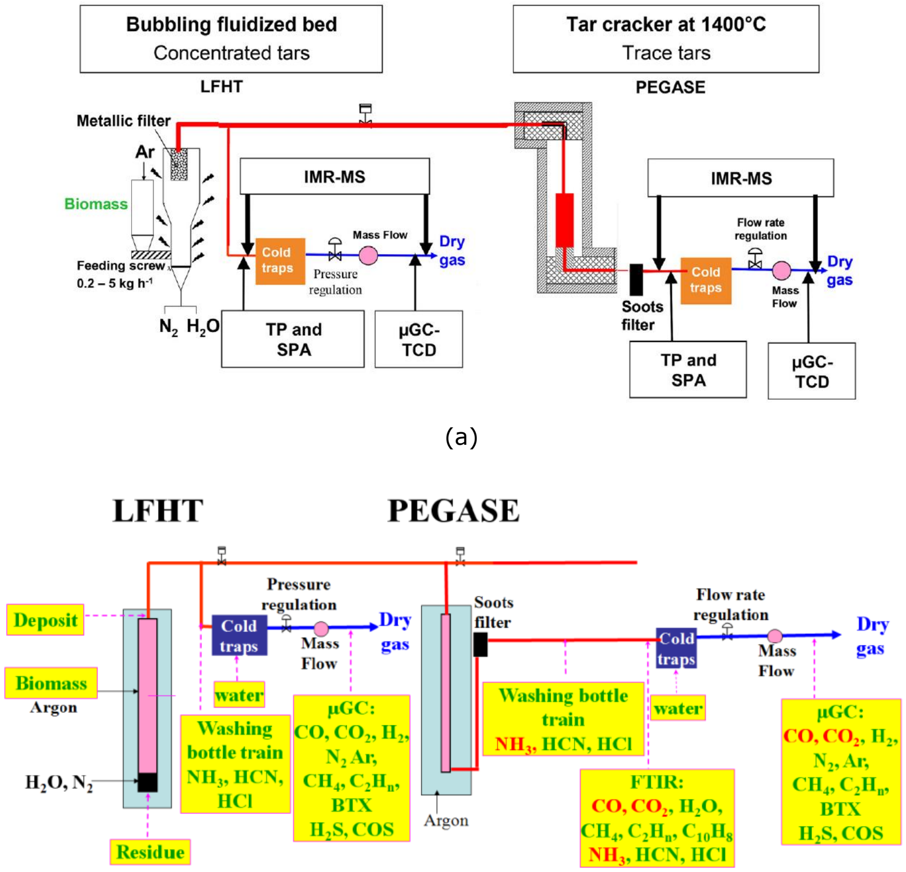
The French Alternative Energies and Atomic Energy Commission (CEA) owns several gasification pilot plants with several types of online and offline gas analysers.

The fluidized-bed facility (LFHT, Figure 94 (a)) has been designed to study biomass pyro-gasification up to 1000°C and 40 bars. The gas reforming reactor (PEGASE, Figure 94 (b)) is applied for the study of the conversion of methane, light hydrocarbons and tars at high temperatures (900-1500°C) up to 4 bars. The two facilities are linked by an insulated line heated at 800°C in order to avoid condensation of inorganic species. The gas reforming reactor (PEGASE) can either work in stand-alone mode with mixtures of pure gases representative of woody biomass pyrolysis at 800°C, or it can work linked to the fluidized bed facility (LFHT) [201].

The exhaust gas of the fluidized-bed facility flows through a metallic high-temperature filter where particulates are removed before leaving the reactor. A ceramic (SiC) filter heated at 900°C at the exhaust of the high temperature reactor captures the soot formed by hydrocarbons conversion. In both facilities, the gas leaving the filter is kept at 600°C until it flows through 2 or 3 cold traps in series, where water and tars are condensed. After the cold traps, the total mass flow rate of gas is measured by a Coriolis mass flow meter. A more detailed description of the facilities can be found in [201]. Figure 95 presents a schematic view of the facilities, including the locations of gas sampling and gas analysis methods.

(a) (b)

Figure 94. Gasification pilot plants at CEA: (a) High-temperature fluidized-bed (LFHT); (b) High-temperature tar cracker (PEGASE). Pictures courtesy of CEA.



(a)

(b)

Figure 95. Schematic view of the pilot scale facilities LFHT linked to PEGASE, including gas analysis points: (a) analysis of tars and permanent gas (IMR-MS, micro-GC, Tar Protocol (TP) and SPA); (b) measurement of inorganics (FTIR, micro-GC, wet chemical analysis) [167].

The Girofle entrained-flow reactor (EFR) pilot unit (Figure 96), which is part of the GENEPI platform [202], is a highly-instrumented facility, that works at high temperature (1500°C) and high pressure (30 bars) with a biomass flowrate (50 kg/h) suitable for performing industrial development. This intermediate scale pilot plant has also been designed to develop and validate several developments, including a solid injection system, an oxy-combustion injection system, refractory liners and materials, ash management systems, water quenching system, and a high-temperature inorganic filtration system.

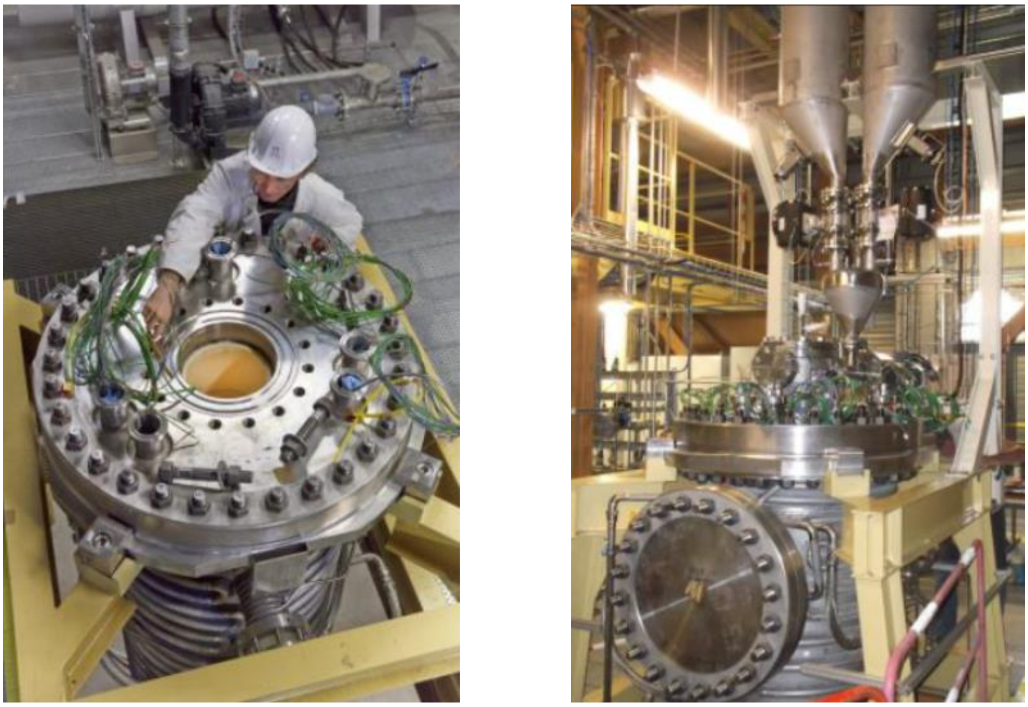

(a) (b)

Figure 96. Entrained-flow reactor (GIROFLE) at CEA Research Centre: (a) top of the reactor; (b) fuel powder injection. Pictures courtesy of CEA.

Gas is online analysed using micro-GC (GC-TCD). The analysers are equipped with 4 columns. The compounds which can be detected include Ar, CO_2, CO, CH_4, N_2, H_2, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_6H_6, C_7H_8, H_2S, and COS. Tar sampling can be performed using the tar protocol method. Solid Phase Adsorption (SPA) sampling, followed by thermal desorption and GC-FID and GC-MS analysis, is also performed in order to quantify tar concentration in the gas. A new method was developed and used here to quantify tars at very low concentrations [203][204]. A colorimeter allows online measurement of H_2S at very low concentrations (0.3 ppm). Washing gas trains are used to measure NH_3 (5 wt.% H_2SO_4), HCN (5 wt.% NaOH), and HCl (water). Liquid solutions are offline analysed by ionic chromatography for inorganic species.

Inorganic species which are soluble in water (NH_3, HCN, HCl) are analysed online by FTIR thanks to a gas cell heated at 150°C to avoid vapor condensation. The FTIR is connected at the exhaust of the high-temperature reactor PEGASE because at the high operating temperatures (1400°C) the gas is clean (no soot, particles or tar) and its IR spectrum is then easy to analyse (no hydrocarbons present such as CH_4, C_2H_2, C_2H_4, C_6H_6, $C_{10}H_8$, etc.). The FTIR spectrometer is configured to be able to measure concentration at a ppmv level as the gas flows through a heated 2-L volume gas cell with an optical path length of 4 m at a 100 NL/h flow rate. The resolution is 0.5 cm^{-1} and the MCT (Mercury Cadmium Telluride) detector is cooled with liquid nitrogen. Every minute a spectrum is acquired (online analysis). An IMR mass spectrometer [35] and an OF-CEAS apparatus are sometimes rented by CEA Grenoble.

3.2.24 Gas analysis by Bioenergy 2020+ - Downdraft gasification for CHP production [205]

Within a 3-year research project, Bioenergy 2020+ performed several measurement campaigns at a commercial small-scale downdraft gasifier for CHP production (nominal electric load of 150 kW_{el}). The overall objective of the project was the development and implementation of novel control strategies to make the gasification system more robust against fluctuations of feedstock properties. During the project, the following gas sampling and analysis techniques were applied (Figure 97):

- Online (every 1 s) measurement of permanent gases in the product gas using a gas analyser (gas monitor). The gas analyser measures CO, CO_2 and CH_4 with an infrared measuring principle (NDIR), H_2 with a thermal conductivity measuring principle and O_2 with an electrochemical measuring principle.

- Online measurement (every 5 s) via FTIR of organic compounds (C_1-C_3), NH_3, HCN, CO, CO_2, CH_4, H_2O, etc.

- Adapted tar guideline method, using 3 double-jacket cooled impingers in a row at -25°C.

- Wet chemical analysis for sampling of H_2S, HCl, NH_3 and HCN (analysed by UV-spectrometry and ion chromatography).

- Flue gas composition (including CO, NO_x, SO_x) at the outlet of the gas engine.

- Complementary to gaseous compounds, feedstock and solid residues were also analysed.

In this project, fast online analysis was crucial to evaluate the stationary and dynamic behaviour of the plant. A special calculation tool (based on Matlab) was developed for the on-site evaluation of the plant behaviour via mass and energy balancing.

Figure 97. Multi-component gas analyser for permanent gases (left) applied at BE2020+: FTIR including gas dilution unit and tar sampling (middle); sample processing for wet chemical analysis (right) [205].

In order to enhance the common methodology and especially the gas sampling techniques, a joint measurement campaign (round robin) was performed by Bioenergy 2020+ and Free University of Bolzano (UNIBZ). Biomass and char samples were simultaneously collected and further distributed between the two research groups for separate lab analysis. In the same way, product gas was collected using a common heated line. After a flow split into two independent lines, product gas was analysed in parallel using different equipment. UNIBZ used micro-GC/FID, whereas BE2020+ applied NDIR, TCD and FTIR analysis. Measurement results of a period of 8 hours of analysis are presented in Figure 98. The separate results of gas analysis are in good agreement, the average error of all gases being than 3% in terms of maximum error recorded; sometimes there is an offset error for methane (CH_4). The maximum CH_4 error was below 7% when comparing the equipment.

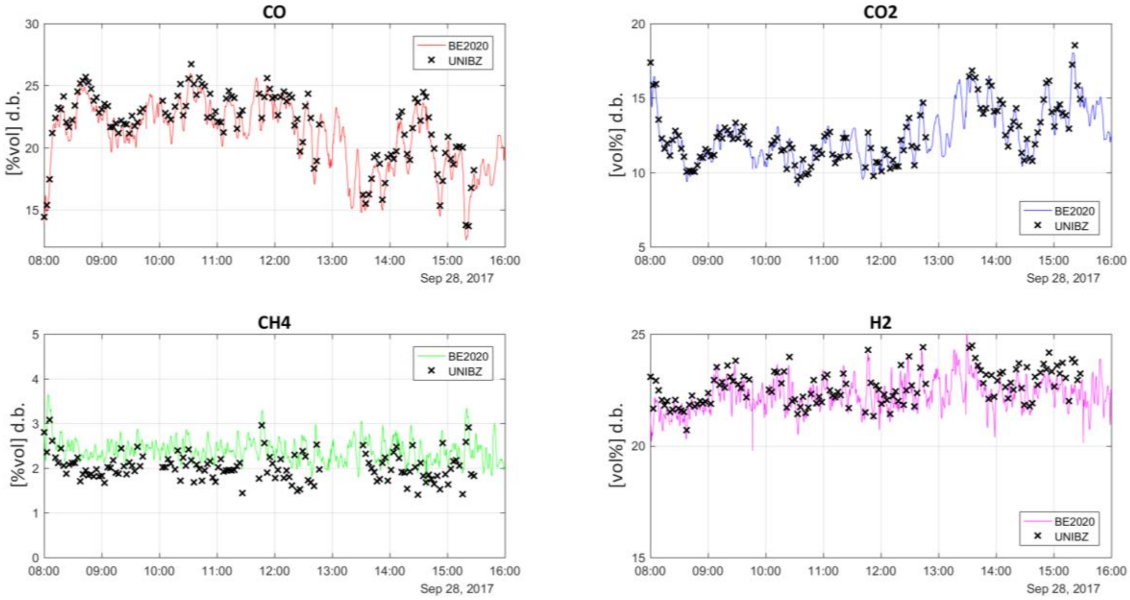


Figure 98. Results from a round robin measurement campaign of UNIBZ (micro-GC/FID) and Bioenergy 2020+ (NDIR, TCD, and FTIR) for comparison of measurement techniques [205].

3.2.25 Gas analysis at ECN part of TNO

The former Energy research Centre of The Netherlands, now called ECN part of TNO since its recent integration within The Netherlands Applied Research Organisation [206], has been extensively working in the deployment of technologies for the efficient thermochemical conversion of biomass and waste, including pyrolysis, torrefaction, gasification and combustion [207]. In the field of gasification and gas upgrading, technologies such as the MILENA indirect gasifier, the OLGA tar removal unit, or the ESME methanation process are some achievements of this extensive development work. At the bioenergy laboratories located in Petten (The Netherlands), several lab-scale and pilot-scale facilities, shown in Figure 99, are available for research work on gasification of biomass and waste.

Table 25 gives an overview of some gas analysis techniques applied at ECN part of TNO (either at the laboratory facilities or in measurement campaigns outside Petten), including corresponding measurement frequency and detection limits. Figure 100 shows as an example the gas sampling point located at the outlet of the pilot-scale MILENA gasifier.

(a) (b) (c)

(c) (d) (e)

Figure 99. Gasification-related research facilities at ECN part of TNO: (a) WOB BFB gasifier, 5 kW_{th} input; (b) MILENA lab-scale indirect gasifier, 25 kW_{th} input; (c) OLGA tar removal unit; (d) ESME methanation lab-test rig; (e) BTX scrubbing unit; (f) MILENA pilot gasifier, 800 kW_{th} input.

Table 25. Overview of main gas analysis capabilities applied in biomass gasification applications at ECN part of TNO.

Gas species	Gas sampling	Instrument	Duration/ frequency	Detection limit
H_2, CO, CO_2, CH_4, O_2	Direct sampling (dry gas)	Gas monitor (see Section 2.2.2)	Continuous	200 ppmv
Ne, Ar/O_2, N_2, CH_4, CO, CO_2, C_2H_2, C_2H_4, C_2H_6, C_6H_6, C_7H_8, H_2S, COS	Direct sampling (dry gas)	Micro-GC (see Section 2.2.2)	5-7 minutes	10 ppmv
H_2S, COS, CH_4S, CS_2, C_4H_4S, C_5H_6S, etc.	Gas bags	GC-FPD (see Section 2.6.2 and Factsheet 15 in Document 2)	15 minutes	0.02 ppmv
C_1-C_6 hydrocarbons	Gas bags	GC-FID (see Section 2.2.3 and Factsheet 14 in Document 2)	30 minutes	1 ppmv
Tar	Tar guideline	GC-FID	30 minutes	0.1 ppmv

Gas species	**Gas sampling**	**Instrument**	**Duration/ frequency**	**Detection limit**
compounds	SPA	GC-FID	2 minutes	0.1 ppmv
NH_3	Wet chemical analysis (HNO_3 solution)	AMFIA	30 minutes	0.5 ppmv
HCN	Wet chemical analysis (NaOH solution)	FIA	30 minutes	0.05 ppmv
HCl, total Cl	Wet chemical analysis (HNO_3 solution) Tar guideline (2-propanol)	Ion chromatography	30 minutes	0.5 ppmv

Figure 100. Gas analysis sampling point at outlet of pilot-scale MILENA gasifier. Picture courtesy of ECN part of TNO.

4. Online analysis of tars and other gas compounds

4.1 OVERVIEW

Due to the large amount of development work that has been devoted and the recent progress in this field in the last years (see for example [40]), this chapter describes some examples of techniques that have been developed for online analysis of tar compounds. Table 26 gives an overview of some online tar analysis techniques, which will be described later in this section. However, there is additional development work ongoing on online detection of other gas species beyond tar compounds that will be also described in this section.

Table 26. Overview of current development work on online tar analysis.

Partner (see Contributing Partners)	**Equipment**	**Status**
BTG, KTH	PID	On hold
CEA	IMR-MS	Commercial
Chalmers University of Technology	High-temperature reactor	Proven in measurement campaign
DTU	UV + IR spectroscopy	Under development, but can be potentially commercialized
ECN part of TNO	Tar dew point analyser MS	On hold
NREL	MBMS	Applied in NREL pilot plants and commercial demonstration plants
PSI	Liquid quench sampling + UV-Vis spectroscopy	Liquid quench in active use and in process of being automated. UV-Vis combination on hold.
TUM TU Berlin	LIFS	On hold
TU Berlin	CON-TAR	On hold
University of Stuttgart	FID difference	Commercial

Partner (see Contributing Partners)	Equipment	Status
UNIBZ University of Erlangen-Nuremberg	LED-induced spectroscopy	?

A relevant aspect in the development of online tar analysis methods is the availability of reliable test gas generators for proper calibration and validation of the techniques. This topic is not covered in this report. A good overview on the topic of test gas generators can be found in [208].

4.2 FID DIFFERENCE, UNIVERSITY OF STUTTGART

The Institute of Combustion and Power Plant Technology (IFK) of University of Stuttgart has developed an automated system for online and semi-continuous monitoring of the total tar content of the gas. The technique is based on the measurement of the difference of a flame ionization detector (FID) of the hydrocarbons present in the product gas [2][19]. The schematic layout of the FID tar analyser is shown in Figure 101. The difference in carbon content contained in the sample gas is measured in 2 sample loops of same volume. The operation of the unit is divided into 2 steps: sampling and analysis. During the sampling phase, the sample loops are filled consecutively with sample gas (Figure 101 left). During the analysis phase, nitrogen flushes the sample gas to the FID analyser. Whereas the gas from loop 1 is flushed over a tar filter, the sample gas from loop 2 is directed unaltered to the FID. As a result, the FID analysis of each loop produces a characteristic peak, displayed in Figure 102. The difference of peak area of loops 1 (peak at the left in Figure 102) and loop 2 (right peak in Figure 102) corresponds to the total tar content of the gas sample. The sampling and analysing phases can be set between 10 seconds and 60 seconds. The system was successfully validated in a 20 kW gasifier (relative deviation of -2%/5% with respect to tar guideline analysis) [19]. The online tar analysis device is commercially available (TA 120-3, Figure 103) [57][209].

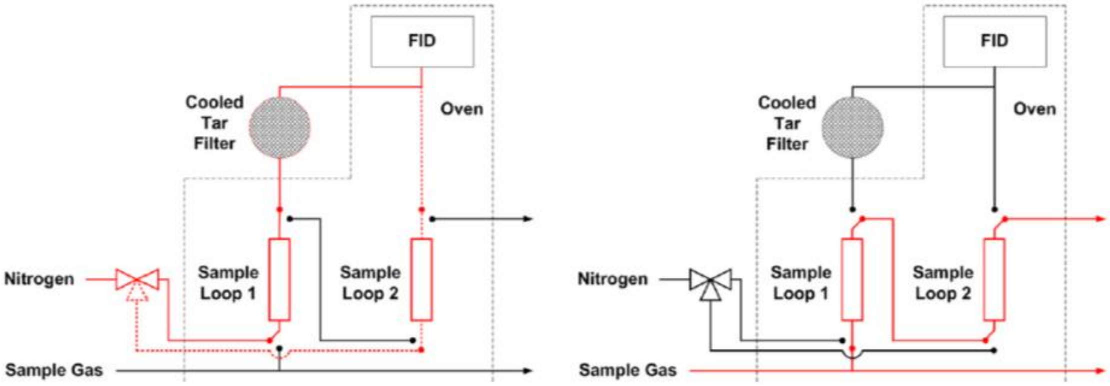


Figure 101. Basic principle of the FID online tar analysis method developed by University of Stuttgart. Left: sampling phase; right: analysis phase [2][19].

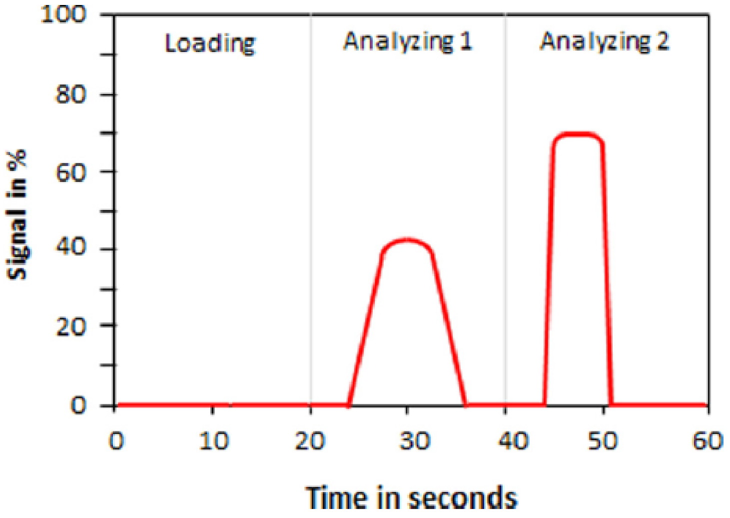


Figure 102. Characteristic peaks derived from FID analysis from the online tar analyser developed by University of Stuttgart. The difference between peak areas corresponds to tar content [2][19].

Figure 103. Commercial online tar analyser developed by University of Stuttgart [57][210][211].

The analyser is equipped with a sample valve which allows sample gas to enter via 4 different inlets: 2 inlets to sample hot product gas, and 2 inlets to calibrate the device before the measurement. Each measurement cycle consists of 2 steps: loading sample gas, and analysis of gas (Figure 102). During the loading, the sample gas from the gasifier enters the apparatus via a heated Venturi pump, and then loaded simultaneously into three sample loops (S1, S2, S3), after having been purified by particle filters. After the loading, the valves switch to analysis mode and the three sample loops are flushed in sequence with a carrier gas (N_2) to the FID for combustion and hydrocarbon quantification. The sample loops 1 and 2 (which have a filter for condensables), measure the content of non-condensable hydrocarbons, while the sample loop 3 (without filter) measures the total content of hydrocarbons. The difference between sample loop 3 and loop 1 or 2 yields the total amount of condensable tar in the sampled gas. Before each measurement, the analyser needs to be calibrated using a gas consisting of CH_4 (5-7 vol.%) in N_2 in order to determine the response factor.

One crucial element of this analyser refers to the selection of the type of tar filter, since the calculation of tars is performed through difference. If tars are not properly adsorbed (saturation problems) or if other components are also adsorbed such as benzene the accuracy of the tar content can be negatively affected. In this sense, research on suitable filters is ongoing.

4.3 CON-TAR, TECHNICAL UNIVERSITY OF BERLIN

The development of this online tar monitoring instrument started in 2008. The basic detection principle of CON-TAR (CONtinuous TAR monitoring/analysis tool) is based on laser-induced fluorescence (LIF). A Nd:YAG Laser with 266 nm excitation wavelength was firstly applied as excitation source [212]. From 2014-2017, within the follow-up BioProGRess project [213], UV-LEDs of different wavelengths were applied as light source in a modified setup for a field deployable tool [214]. The main focus was to build a robust tool, with as little operator input and maintenance as possible. The system went through several adaptations in the heated section with the tar-loaded gas, the gas cell with the optical access points, the gas flow to the cell and the gas flow control by valve and jet pump, and finally a combustion units for the removal from the spent sample gas of tars, CO and other combustible gases. The section containing the optical instruments and electronics was temperature-controlled. As auxiliary gases, CON-TAR uses pressurized air (for the jet pump ad the catalytic oxidizer of the off gas), and 1 L/min N_2 to purge the optical window to avoid condensation. The setup includes a lambda probe that indicates whether the gas is properly sampled [60]. This monitoring tool, in the configuration applied at the GoBiGas plant, provides an online qualitative measurement of the total level of PAHs (naphthalene and larger compounds). With appropriate calibration of the most abundant individual tar species in the gas, quantification is claimed to be possible.

Figure 104. CON-TAR online tar measurement unit at the GoBiGas plant. Picture courtesy of Goteborg Energi [60].

A demonstration unit of the CON-TAR equipment with UV LEDs (Figure 104) was tested for more than 400 hours at the new gas sampling system of the GoBiGas plant (see Section 3.2.2 for more details about the sampling system implemented in the plant). A small stream of the hot, tar-loaded product gas is led by heated lines into the hot measurement cell where tar species are detected. The measurement cell and the optics are built in a metal box (located on the floor in the centre of Figure 104), whereas the electronics and controls are in the compartment on the upper left. The unit allowed the online determination of total amount of tar (naphthalene and larger components) around the gas cooler, the gas filter and the RME scrubber of the plant, as shown in Figure 105. CON-TAR provided valuable information to the plant operation (fluctuation of the tar content when the gas filter is pulsed). This type of information about dynamic performance could not have been properly observed only with offline tar analysis [60].

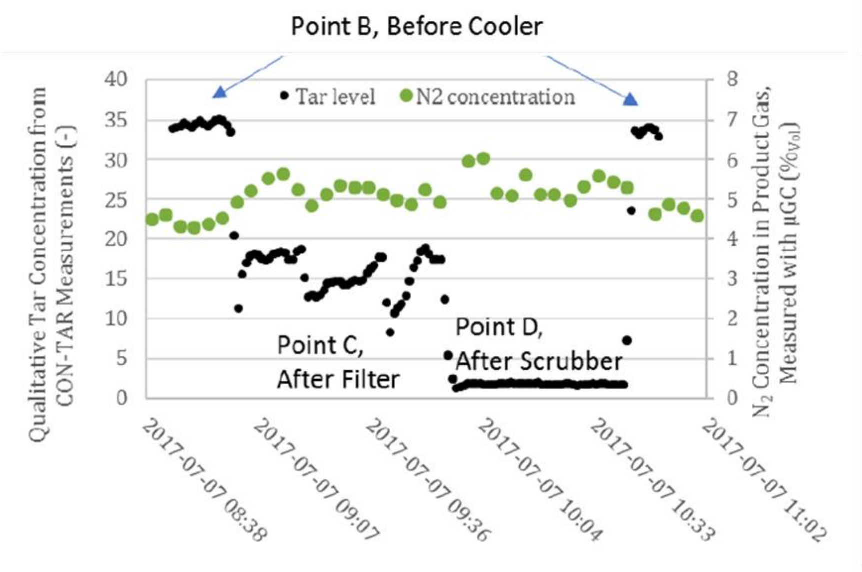


Figure 105. Results of testing of CON-TAR prototype at GoBiGas plant for qualitative online measurement of total tar content [60].

Within the NWG-TCKON project (2012-2018), several possibilities to obtain more detailed information on individual tar species from the overall fluorescence signal in the hot gas phase were examined. A wavelength tuneable Optical Parametric Oscillator (OPO) laser was used as light source in the laboratory experiments. By scanning wavelengths, so called excitation-emission matrices can be obtained. These provide a fingerprint of the tar-matrix in the gas. With this knowledge also simpler devices e.g. with multiple LEDs could provide additional information on the tar composition. This cannot be as detailed as any chromatographic or mass selective separation step, but it could still provide online and nearly real-time information from the respective part of the plant. Moreover, the fluorescence decay times among the aromatic molecules differ. This is another feature that one could make use to differentiate among or to monitor individual tar species.

For this kind of work, well-working test gas generators are a must. In these works, a syringe pump and evaporator were applied. The monitoring tool was compared with the one described in the tar analyser from University of Stuttgart, described in Section 4.2, when operated on a test gas generation system applying ethene pyrolysis [52].

The work at TU Berlin on this topic has come to an end. Nevertheless, there are activities of former group members to make use of the gained experiences and to bring out an instrument on this basis.

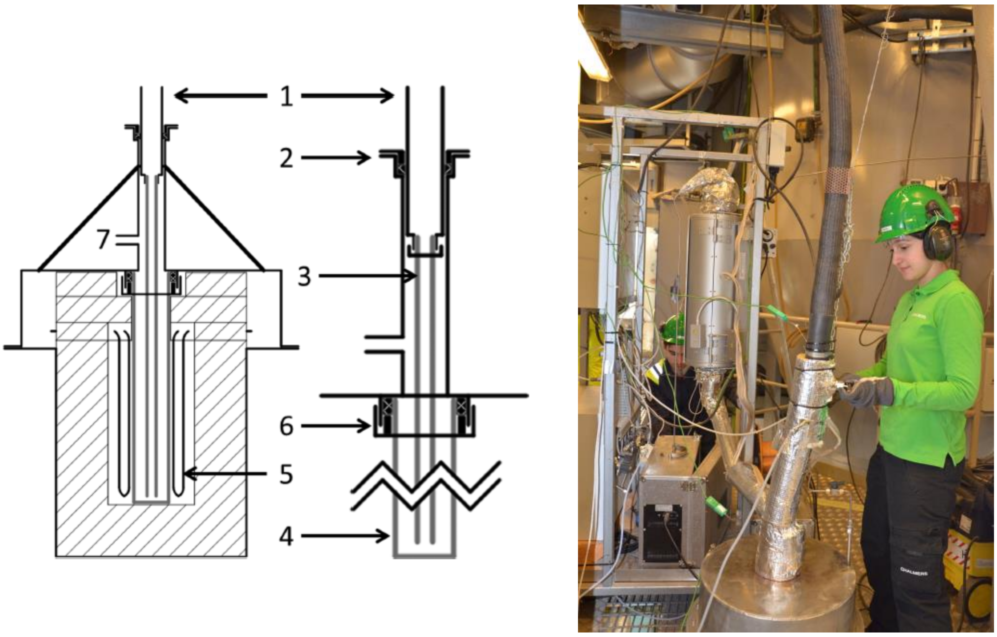
4.4 ONLINE MEASUREMENT OF CARBON CONTENT IN PRODUCT GAS, CHALMERS UNIVERSITY OF TECHNOLOGY

There are 2 main contributions to the carbon content contained in gasification gas: that contained in the permanent gas (which can be measured online using for example micro-GC or NDIR detectors), and the carbon contained in (condensable) tars, which is usually measured offline using for example the tar guideline or SPA methods. That results in inaccurate quantification of cold gas efficiency, carbon conversion and balances, thus making it difficult to follow rapid variations in the gasification process.

A solution to the challenge of accurate mass balances in gasification processes was ideated by Chalmers University of Technology, which consists of quantifying the total amount of carbon contained in the gas. When used in parallel with conventional online gas analysis (e.g. micro-GC), the difference between both systems, corresponding to the C/H/O contained in tars, provides a fast way to monitor the C, H, O, and N molar balances in the gasifier, thus allowing tracking of rapid variations in the process.

The determination of the carbon (as well as H, O, and N) content in the gas can be performed either by combusting the gas sample prior to analysis [215], or by applying high-temperature thermal cracking of tars plus further gasification of carbon [216]. The latter concept (called HTR or High-Temperature Reactor) overcomes some limitations of the combustion concept, namely the inaccuracy derived from the diluting effect of the nitrogen from the oxidising air, or the safety issues related to the use of pure oxygen as oxidant. However, carbon determination via combustion offers the advantage of enabling the possibility of online moisture determination of the gas, thus allowing measuring the total content of oxygen and hydrogen in the gas [216].

The HTR device is schematically shown in Figure 106. It consists of a ceramic reactor within an oven placed inside a gas-tight steel casing. The inlet gas entering at 350°C is introduced to the top of the reactor via an adapter (1) connected to the reactor by a flange (2). The reactor is an alumina tube (3), which has a lower part consisting in a closed-bottom tube of a larger diameter (4). The whole reactor is surrounded by oven heating elements (5). The gas exits the reactor via the outlet (7). The outlet gas is then derived to an analysis unit (e.g. a micro-GC).



(a) (b)

Figure 106. Schematic of the HTR (High-Temperature Reactor) developed by Chalmers for the online determination of C, H, O and N in the product gas [216].

Before operation, the HTR needs to be started up by applying a temperature ramp a few hours before operation to avoid cracking of the alumina tube due to thermal stress. The system was validated in the Chalmers 2-4−MW dual fluidized bed gasifier [216] (see Section 3.2.19). The results showed a very high degree of conversion of hydrocarbons heavier than methane. The level of tar exiting the HTR was negligible compared to the value obtained using the SPA method, thus revealing the effective conversion (reforming) of hydrocarbons into H_2 and CO.

4.5 GC-FID FOR ONLINE TAR ANALYSIS, TUD

Technical University Delft (TUD) studied the application of GC-FID for the online measurement of tar compounds in the framework of the BRISK project [33]. For this application, the GC unit was equipped with a heated gas injection loop set at 175°C connected to the gas sampling line, which enabled the injection of the product gas in a continuous mode. The developed analysis method was tested at the CFB gasifier located at TUD laboratories. During the gasification tests it was observed that the base line of the GC-FID chromatograms was not smooth and had a significant amount of noise, which was attributed to the large amount of water contained in the product gas. This noise negatively affected the quantification, which led to the need for manual correction, thus complicating the analysis procedure [33]. Moreover, the existence of non-heated lines in the setup led to difficulties in the calibration of naphthalene and other PAH compounds (not reproducible results). On the other hand, the temperature of the heated injection loop was too low to prevent condensation of tars, which resulted in the decrease of sample flow over time. This issue was overcome by increasing the temperature of the injection loop to 300°C [33].

4.6 ONLINE TAR MEASUREMENT BASED ON IMR-MS, CEA

The French Alternative Energies and Atomic Energy Commission (CEA) has adapted ion molecular reaction mass spectrometry (IMR-MS) for online tar measurement [217]. In IMR-MS, the primary ion source is run with an inert gas (Hg, Xe, Kr) instead of a reactant gas (such as in Chemical Ionization Mass Spectrometry). The inert gas is ionized by electron impact (EI) in the chamber of primary ion ionization. The primary ions are led to the reaction chamber through a high frequency octopole ion guide. Here the primary ions react with the sample gas. The chamber of primary ion production and the reaction chamber are separated. The ion molecule reaction takes place under vacuum (approximately 10 mPa). The ionized sample gas is conducted to a quadrupole and a downstream counter for mass separation, detection and quantification. More details about this technique can be found in Factsheet 19 of Document 2.

The IMR-MS apparatus was tested at a fluidized-bed gasifier [217]. A heated low-pressure capillary (operated at 180°C) was used to sample the gas. Measurements with both wet gas and dry gas from steam gasification were performed. In the case of wet gas, a prior dilution of the product gas with nitrogen was applied. The dilution is a disadvantage, since it leads to less consistent results (values close to detection limit of the apparatus). The masses corresponding to benzene, toluene, thiophene, phenol, indene, acenaphthylene, biphenyl + acenaphthene, fluorene, phenanthrene + anthracene are well defined. Other masses corresponding to some inorganic gaseous species such as H_2S, NH_3 C_2H_4 and thiophene could also be detected by the IMR-MS apparatus.

Although the first validation tests were promising, this technique needs still some improvements. For example, the measurement of COS, H_2S, HCl and NH_3 is challenging when applied to wet gas due to overlapping in the signal. Moreover, it is an expensive apparatus [217].

4.7 PHOTO IONIZATION DETECTOR (PID), BTG AND KTH

This technique, jointly developed by BTG (The Netherlands) and KTH (Sweden), is based on the excitation of gas compounds by photons generated by an ultraviolet lamp filled with a gas (xenon, with an ionization potential of 8.4 eV). The charged molecules generate in turn a current that is proportional to the concentration of the compound in the gas [59][50]. Depending on the ionization potential applied, different compounds can be detected. One of the advantages of the PID technique is the linear response factor of the aromatic compounds. Moreover, it is very sensitive to low concentrations (<10 mg/Nm^3) and has been validated against other measurement techniques like SPA. However, PID cannot quantify individual tar compounds in the tar mixture. Fouling of the excitation chamber, which decreases the PID response over time, is a challenging issue which results in the need for periodic cleaning of the equipment. More details about the PID tar analyser can be found in Factsheet 32 of Document 2.

4.8 MOLECULAR BEAM MASS SPECTROMETRY (MBMS)

This analysis technique is a type of mass spectroscopy which can be applied for the online measurement of tars (US National Renewable Energy Laboratory, NREL), or for the analysis of inorganic compounds present in the product gas (NREL, Jülich Forschungszentrum).

The MBMS online analyser has been extensively used by NREL for more than 30 years, including in measurement campaigns at the Battelle Columbus Laboratory indirect circulating fluidized-bed gasifier, at the Gas Technology Institute (GTI) pressurized fluidized-bed gasifier [39], and more recently at the Rentech’s natural gas-to-liquids demonstration unit [61]. When applied to online analysis of tars, the MBMS can provide real-time and robust monitoring of hot, raw product gas;

near-universal, reproducible and stable detection with sensitivity of approximately 1 ppmv. However, it is a complex system, and the quantification can be cumbersome, since it requires injection of standard for each target species and good measurement of wet gas volumetric flow. The analyser compares well with the Tar Guideline, but the estimation of total gravimetric tar is difficult due to the problematic injection of heavy tar standards into the hot oven and capillary plugging. Although the MBMS analyser is commercially available, it is quite expensive (~ $300 000). Moreover, there is still room for improvement in terms of size, weight and energy efficiency [61].

On the other hand, MBMS has been applied at Jülich Forschungszentrum for the study of the release of inorganic trace elements during gasification [133]. For this application, a relevant issue to consider is the potential interference of organic compounds, which can negatively affect the accuracy of the measurement. For this reason, the MBMS equipment was located at the end of a pipe which acted as thermal cracker in order to destroy the organic compounds present in the gas that could potentially overlap with the target gases. More details about the MBMS technique can be found in Factsheet 28 of Document 2.

4.9 LASER-INDUCED FLUORESCENCE SPECTROSCOPY (LIFS), TUM

This laser spectroscopic technique, developed by Technical University Munich, is able to identify single compounds in complex tar mixtures and is used for the online and continuous monitoring of tar produced from a gasifier. The LIFS can quantify several individual tar compounds, including phenol, (o/m) cresol, toluene, styrene, o-xylene, indene, biphenyl, anthracene, fluorine, naphthalene, fluoranthene, pyrene and perylene [58].

A schematic diagram of the LIFS apparatus is displayed in Figure 107. The system consists of a N_2 pulsed laser (excitation source) which emits light at a wavelength λ = 337.1 nm, and power of approximately 10 mW, a CCD camera with an external image intensifier, and a spectrophotometer. The product gas is introduced via heated lines to an electrically heated measurement cell (operating at 300°C) to avoid tar condensation. The spectrophotometer and the CCD camera are placed perpendicular to the excitation source in order to measure the emitted light from the gas in the cell.

The LIFS analyser needs to be calibrated before the tar measurement. This is done with a tar mixing station, which produces a well-defined mixture of tar compounds. The generated tar concentrations are validated by applying a tar protocol measurement downstream the tar mixing station. The calibration of the LIFS system consists of the detection of the fluorescence signal emitted by the individual target tar compounds. Several spectra of individual tar compounds and test mixtures at different concentrations are recorded. During both calibration and analysis, the temperature of the measurement cell as well as the parameters of the optical setup (gain, width and delay of the CCD camera, data acquisition timing) are kept constant. A linear mathematical model based on partial least squares fit is applied to evaluate the signal from the mixtures [58].

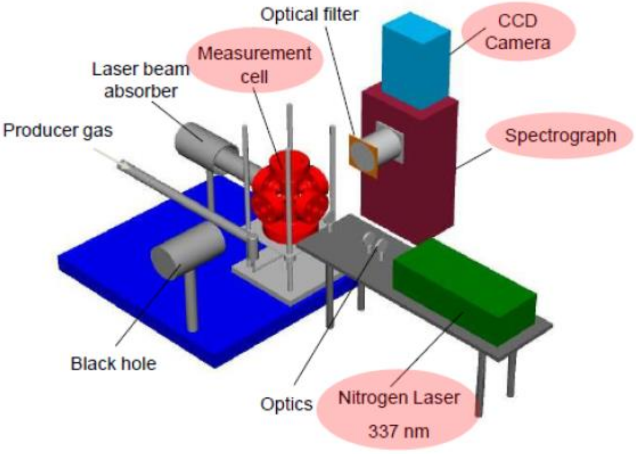


Figure 107. Laser Induced Fluorescence Spectroscopy [58].

4.10 LIQUID QUENCHING + UV-VIS SPECTROSCOPY, PSI

The Paul Scherrer Institute (PSI) is working on the development of an online UV-Vis method to monitor tar compounds. Unlike other online tar techniques, a liquid quench sampling system is implemented as a first step. The liquid quench system transfers condensable gas species, including tars, into an organic solvent flow whose absorbance is measured. Compared with gas-phase calibration, the measurement in the liquid phase used in this technique allows easy calibration, where less complex instrumentation is required. As a second step, the liquid samples were analysed by UV-Vis spectroscopy (selected as a quick and robust, yet economical technique) [63].

The UV-Vis analysis was tested both using model compounds and with real product gas. Figure 108 shows an example of spectra measured before and after an RME scrubber (tar removal unit). The spectra reveal a complex mixture of hydrocarbons. The plot allows for a qualitative analysis of the tar composition as a function of time. Absorption features in the range 250-290 nm indicate the presence of light aromatic compounds. Moreover, features at 276 nm and 287 nm suggest the presence of naphthalene at high concentrations. The high spectral overlap at lower wavelengths significantly complicates the quantification of further compounds. In some cases, the maximum absorbance of the instrument was exceeded. Therefore, in those cases in which a complex tar composition is expected (such as in raw product gas), quantitative analysis is not possible due to the high number and spectral overlap (co-linearity) of tar compounds. Because the product of concentration and extinction coefficient of tar compounds can span over orders of magnitude, tar compounds with high absorbance might mask the presence of tar compounds with smaller absorbance values. In such situations this method cannot replace more expensive online analytical tools, but it can provide qualitative information for process monitoring. Quantitative analysis becomes feasible when the number of tar compounds is limited (e.g. after tar removal) [63].

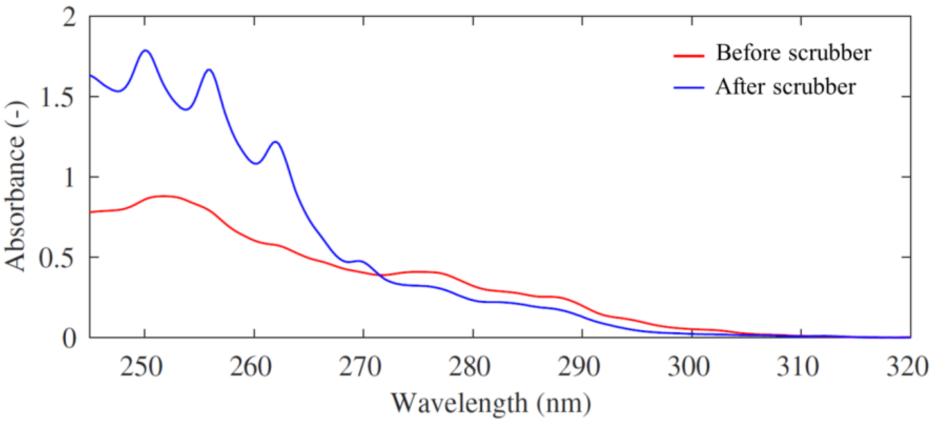


Figure 108. Spectra obtained at PSI before and after an oil scrubber applying liquid quench sampling coupled to UV-Vis spectroscopy [63].

4.11 UV + IR SPECTROSCOPY, DTU

Some compounds (e.g. C_xH_y, oxo- or PAHs) have very characteristic absorption features in IR and UV spectral ranges which can be used for their monitoring and process control. Technical University of Denmark (DTU) applies UV and IR spectroscopy for online measurement of tars. Product gas (either through a particle filter at 300°C or without particle filter at 500°C) is diluted with pre-heated N_2 before entering the analysis equipment [65]. The whole system is heated at 150°C [122]. The gas sampling measurement system is shown in Figure 109.

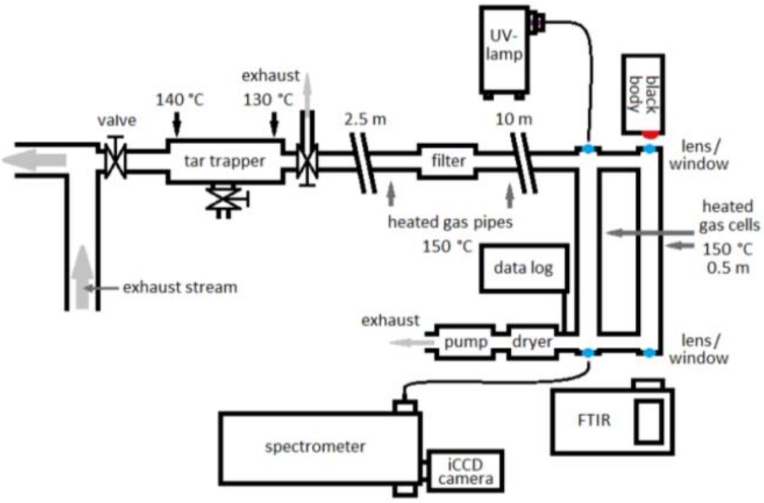


Figure 109. Gas sampling system used by DTU for online UV/IR measurement of tars and other gas compounds [11][65][219].

Optical measurements were applied at a measurement campaign at the Pyroneer [65], the LT-CFB and the Viking gasifiers [122]. More details about these campaigns can be consulted in Section 3.2.6 of this document. The UV absorption spectroscopy measurements showed a strong UV absorption of PAH/tar compounds in the range of 200-300 nm. Phenol (representative tar compound of low-temperature gasification processes) was determined as the main gas component in the differential (DOAS) spectrum. Phenol measurements have also been performed in-situ (that is without gas extraction), as shown in Figure 110. The optical windows of the setup are purged with N_2. The measured phenol concentration in the gas at about 400°C was found to be higher than that measured with gas extraction and gas sampling in pipettes for GC-MS analysis.

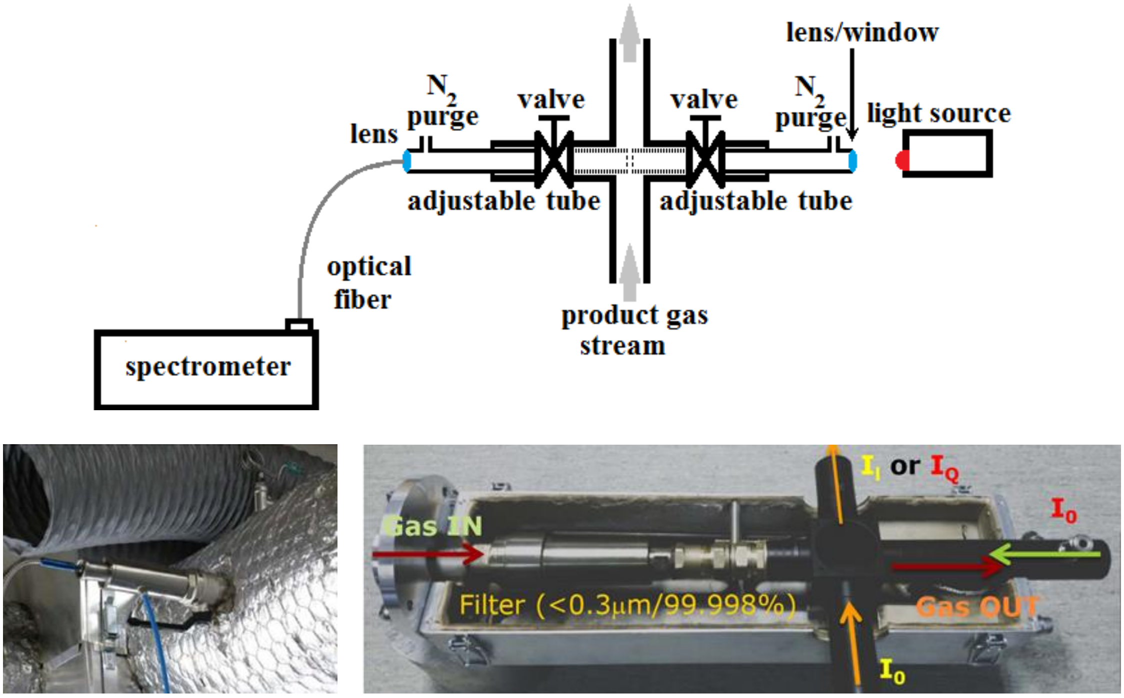


Figure 110. In-situ UV measurement of tars (no gas extraction) by DTU [11][65][122][219].

Further extension of the DTU's measurement capabilities into far-UV spectral range (120-200 nm) has been carried out. This allows one to select sub-spectral ranges where absorption is dominated either by absorption of saturated, unsaturated (double/triple C-C bond and C=O) hydrocarbons, BTX or tars. The technique is suitable for both major, minor and traces gases analysis in various (oxygen-free) gasification processes [220].

4.12 TAR DEW POINT ANALYSER, ECN PART OF TNO

The tar dew point is the temperature at which the gas gets saturated with tar. This is a relevant parameter in (biomass) gasification processes, since it indicates whether problems (fouling due to tar condensation) can be expected. The tar dew point depends mainly on the composition of the tar produced. For example, the presence of small amounts of heavy PAH compounds can dramatically influence the resulting dew point of the tar mixture [38]. Therefore, the (online) measurement of the tar dew point seems an interesting approach to directly track the operational risk of the tar content of the product gas.

ECN part of TNO and Mitchell Instruments jointly developed a tar dew point analyser by adapting existing hydrocarbon dew point detectors used in natural gas applications to gasification applications [221]. Validation tests of the analyser revealed that the shape of the dew point curve of biomass tar is similar to that of the dew point of hydrocarbons contained in natural gas. Thus, the analyser can be also applied in biomass gasification applications. The tar dew point analyser can properly quantify the tar dew point of tar within a broad range (150-500 mg/Nm^3), which is equivalent to a range of 25-170°C. However, the operating temperature of the analyser is restricted by the thermal resistance of the fibre optics (approximately 200°C), which means that the equipment is not suitable for raw product gas. Irreversible fouling of the sensor by tar polymerization is another potential risk for measurements at high temperature. Further information can be found in Factsheet 42 of Document 2.

4.13 DIODE LASER SPECTROSCOPY, NREL

This technique (Figure 111), currently under development by the US National Renewable Energy Laboratory (NREL), is based on near-IR absorption spectroscopy. It has a detection limit of 0.1 ppmv, and a response time of approximately 2 seconds. The main limitation is related to absorption interferences, especially water vapor [61].

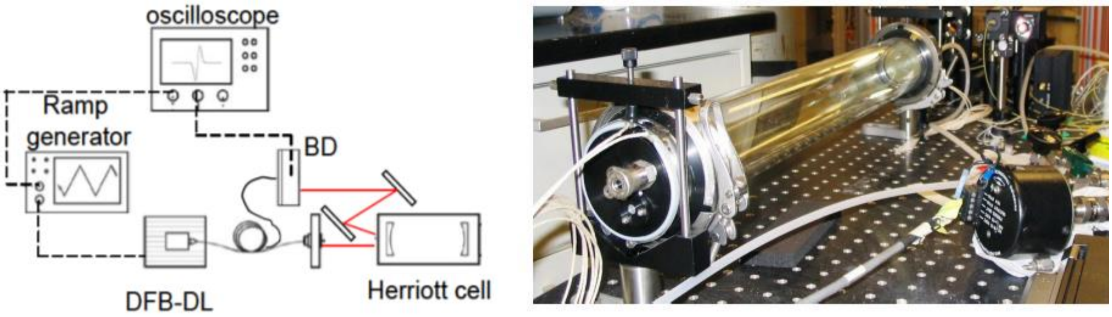


Figure 111. Diode laser spectroscopy developed by NREL: BD – balanced detector, DFB-DL – distributed feedback/ diode laser [61].

4.14 MASS SPECTROMETRY (MS)

In 2015, ECN part of TNO tried to implement mass spectrometry for the online measurement of tars. The equipment was tested in 2 tests, one at lab-scale [162], and one at a commercial gasification plant located in Portugal [163]. For a first proof-of-concept, the MS equipment was placed after the OLGA tar removal system during a duration test at ECN laboratories. At the sampling point, a gas pump (200-500 mL/min) was placed after a quartz filter. A slipstream of the pumped gas (1 mL/min) was fed to the MS via a fused silica capillary. In order to avoid the clogging of the capillary due to particles or aerosols, a particle trap was implemented after the quartz filter. The whole sampling line was traced at 120°C. The selected mass/charge ratios selected for the measurement of tars included benzene (m/z = 78), toluene (m/z = 91), phenol (m/z = 94), naphthalene (m/z = 128), and phenanthrene/anthracene (m/z = 178). The MS pressure was also monitored. The MS pressure is an important signal to consider, since an increasing vacuum would imply a lower gas flow entering the MS unit, thus indicating plugging either in the capillary or in the MS. Therefore, stable MS pressure signal indicates proper measurement. The signals obtained during the first laboratory test are plotted in Figure 112. During the experiment, no clogging of the capillary was observed, which was a promising result. However, since no calibration was performed, no quantification of the tar concentration was possible. Another issue to take into account is the eventual interference of the different compounds with the mass fragments of each other. For example, besides toluene, there are more compounds with mass fragment of 91, mainly xylenes. Although there is less interference expected between phenol and naphthalene, this cannot be excluded.

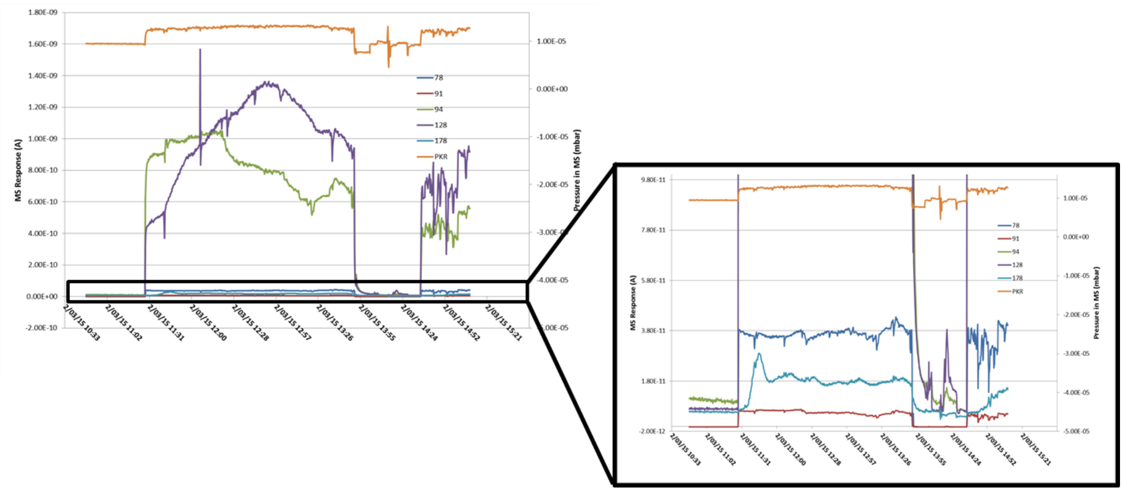


Figure 112. MS signals during online tar analysis at a lab-scale test at ECN part of TNO. Legend: m/z = 78 – benzene; m/z = 91 – toluene; m/z = 94 – phenol; m/z = 128 – naphthalene; m/z = 178 – phenanthrene/anthracene (left axis); PKR: MS pressure (mbar, right axis) [162].

After the first successful trial at lab-scale, the MS equipment was implemented during a test campaign performed at the Iberfer gasification plant (located at Tondela, Portugal). Further details about the results can be found in Section 3.2.7.

4.15 HIGH-RESOLUTION MASS SPECTROMETRY

NREL is working on the application of high-resolution magnetic sector mass spectrometry (Figure 113) in order to be able to analyse in real-time syngas impurities such as NH_3, HCl, and H_2S at very low levels. The inlet system has been modified to enable continuous monitoring of product gas. The apparatus can measure in the range of 1-3000 amu, with sensitivity of 30 pg/μL (ppt level). However, the capillary inlet may limit the throughput of high-mass compounds. Other limitations of this technique include the stability of the magnet with ambient temperature, and the robustness of the ion source [61].

Figure 113. High-resolution mass spectrometer installed at NREL laboratories [61].

4.16 TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY (TDLAS)

Laser absorption spectroscopy (group which encompasses several variations, including TDLAS) has been identified as an attractive option for the online, non-intrusive measurement of a broad number of compounds present in gasification gas. More details about TDLAS can be found in Factsheet 43 of Document 2.

University of Stanford and University of Utah have jointly worked on the development of TDLAS units for the online measurement of syngas components. The prototype, shown schematically in Figure 114, was applied for the online measurement of CO, CO_2, CH_4 and H_2O in coal entrained-flow gasification [14]. For this application, 4 fibre-coupled lasers were tuned to transitions near 2325, 2017, 2290 and 1352 nm.

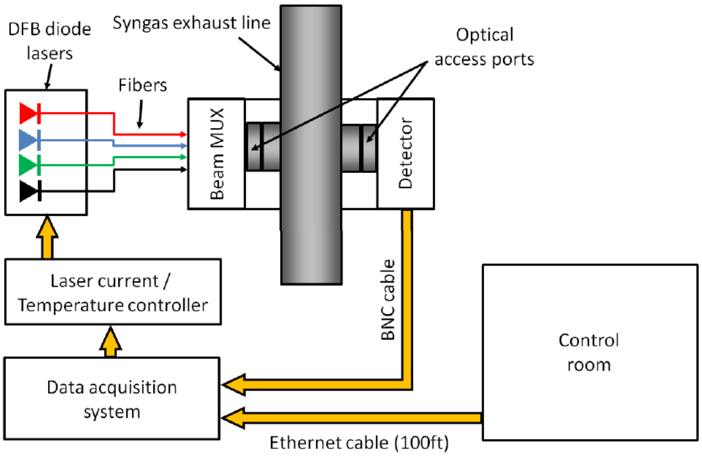


Figure 114. Schematic diagram of TDLAS unit developed by University of Stanford and University of Utah and implementation in gasification line [14].

The main challenges reported for in-situ application of TDLAS include the collision-broadening of the absorption spectrum at elevated pressure (10-50 atm), and the transmission attenuation by particulate scattering [14]. The former might not be of application at most of current biomass- and waste gasification processes, which most of the times take place at pressures well below 10 bar. The implementation of TDLAS in biomass gasification plants might entail additional challenges to those encountered in clean syngas from entrained flow gasification (with a relatively simple composition).

5 Outlook of joint research activities in gas analysis

Gas analysis can play an important supporting role in the commercial deployment of biomass- and waste gasification processes. With this view in mind, one of the objectives of this guideline report is to further promote the collaboration and the exchange of knowledge among researchers in the field of gas analysis. This chapter gives a glimpse of some recent and current joint research activities related to measurement of gas compounds in gasification applications in order to identify opportunities for future collaboration.

5.1 THE GAS ANALYSIS WORKING GROUP (GAW)

The GAW is an international working group which aims at the exchange of experiences in the fields of sampling and analysis of compounds present in gases from thermochemical (pyrolysis gas, product gas, conditioned synthesis gas) and biochemical (biogas from anaerobic digestion) processes. The Gas Analysis group started its activity in 2010 in a workshop as part of a German research project, and since 2011 [222], regular international workshops and webinars are held, where the status and other relevant issues in the field on gas analysis are discussed. The approach of the group is based on the establishment of a collaborative network for the sharing of knowledge on gas analysis. Besides the workshops and webinars of the working groups, the information is also disseminated at their website [5] and wiki [223]. The active collaboration of the GAW coordinators and members has been crucial in the preparation of this IEA special report, which might in turn broaden up and reinforce the GAW network.

As an example of research activities supported by the Gas Analysis Group, a joint measurement campaign is planned in July 2018 at University of Stuttgart laboratories. The experiment was carried out at the 25 kW_{th} BFB gasifier using sewage sludge as feedstock, with focus on the measurement of N- and S compounds in the product gas.

5.2 BRISK AND BRISK-2 PROJECTS

A good example of recent collaborative research in the field of gas analysis can be found in the European FP7 BRISK project [71][224], which started in 2011 and finalized in 2015. Within WP7 of the project, new developments in gas analysis techniques applied to thermochemical conversion were investigated. Particle measurement was studied within WP6 (see Section 2.12.3). Moreover, several measurement campaigns (round robins) were performed in 2013-2015 in order to compare the performance of existing diagnostic techniques (FID, MS, PFPD and SCD detectors) for tar and sulphur compounds [33]. The first of these campaigns took place at the 100 kW_{th} steam-oxygen CFB gasifier at Technical University Delft in June 2012, with TU Delft (host), PSI and ECN as participants. The second host site measurement campaign was performed at PSI laboratories in Switzerland in November 2013 using product gas from a 5 kW fluidized bed gasifier. Different partners tested their sampling and analysis equipment for measurement of sulphur compounds: PSI (host), TU Delft, Tübitak Mam, Bioenergy 2020+, and ECN. The third campaign (October-November 2014) was performed at ECN (SNG duration test). Tar samples collected by ECN were then distributed for analysis to several partners within and outside the project consortium. The lessons learned from these round robin campaigns are discussed in [225]. Figure 115 and Figure 116 show as an example the planning and execution of the joint measurement round robin at PSI.

The follow-up H2020 BRISK-2 project was started in May 2017 [226]. Within WP6 of the project, research will continue in the field of online monitoring of product gas and pyrolysis gas, and the development of protocols for the measurement of trace compounds (including light tar compounds, S- and N- compounds, etc.). The validation of selected measurement techniques will be performed in joint measurement campaigns and round robin tests. Besides the Joint Research Activities, BRISK-2 offers Transnational Access for users to research facilities offered by the project partners [227]. The Transnational Access of BRISK-2 might be a good opportunity for the testing and validation of novel gas analysis techniques using top European research infrastructure.

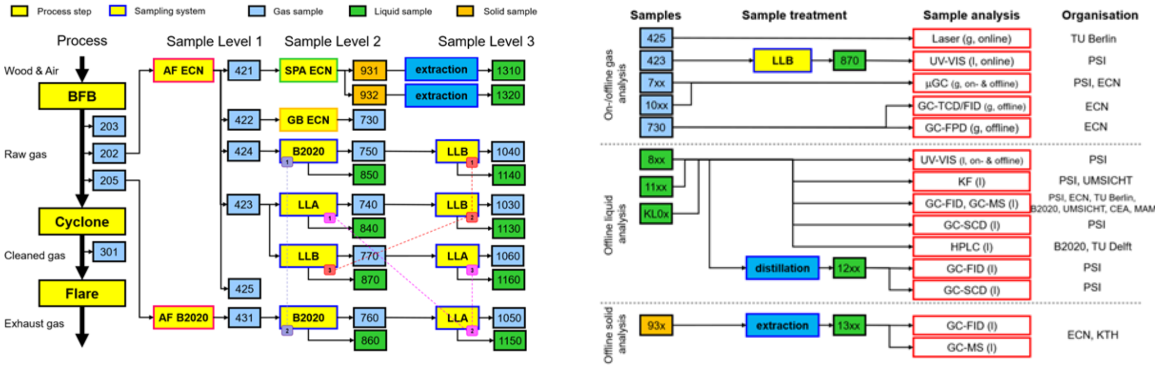


Figure 115. Configuration (left) and sample treatment (right) during gas analysis round robin campaign at PSI, November 2013 [225].

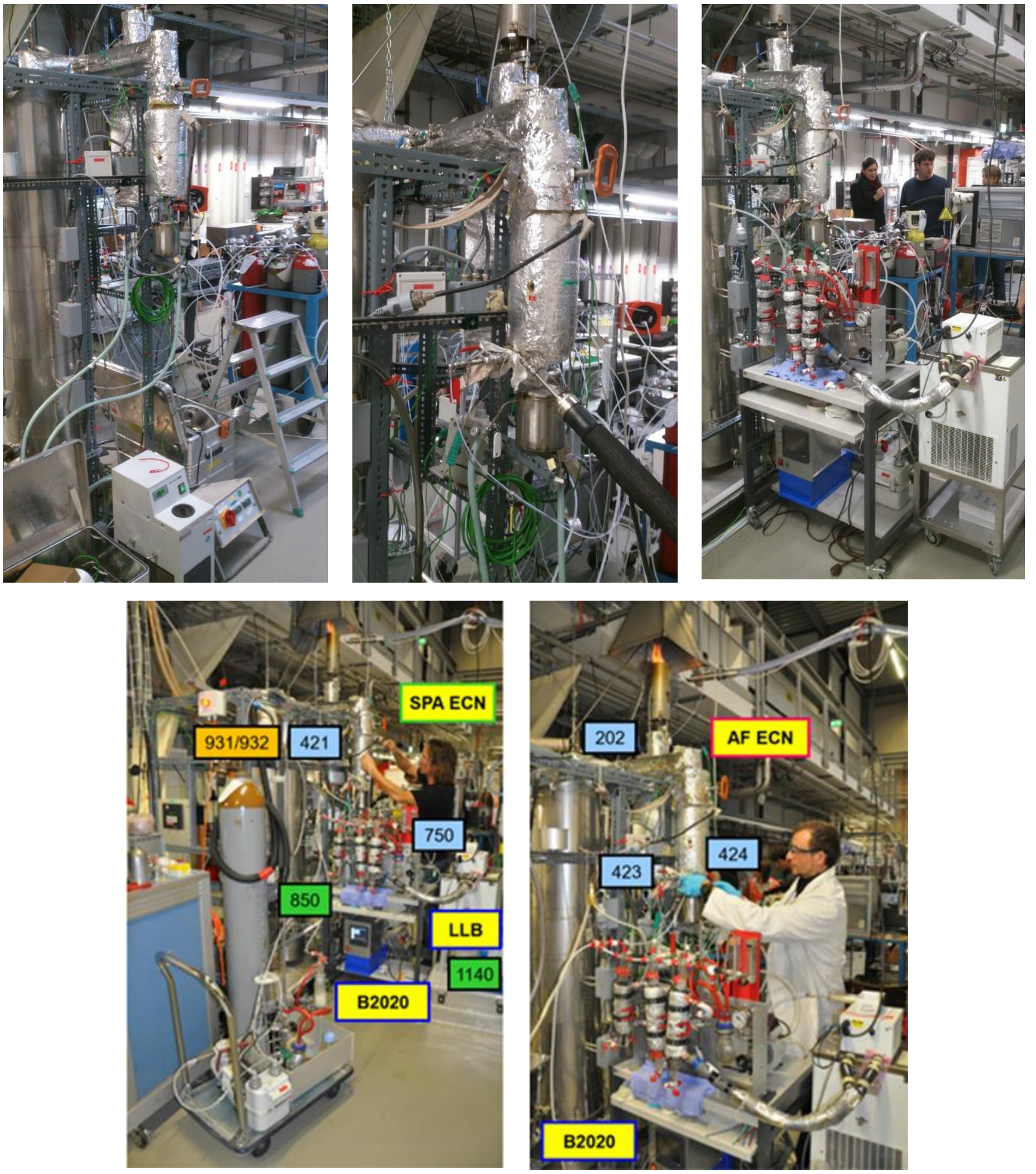


Figure 116. Pictures from joint measurement campaign of BRISK WP7 at PSI laboratories, November 2013 (pictures from [225] and ECN part of TNO).

6 Conclusions and outlook

Gasification is generally acknowledged as one of the technologies that will enable the large-scale production of biofuels and green chemicals from biomass and waste. One of the main technical challenges associated to the commercial deployment of biomass gasification is the cleaning and upgrading of the product gas. In this sense, the development and implementation of inexpensive yet accurate gas analysis techniques to monitor the fate of gas contaminants will play an important role in the commercialization of biomass and waste gasification processes.

The present IEA special report (which is composed of 2 complementary documents) has been the result of a joint collaborative effort of a large pool of experts in the field of gas analysis and biomass gasification. This guideline compiles the experiences of the contributing partners in the field of gas analysis applied to gasification in order to promote the exchange of knowledge, thus facilitating advances in the development of fast, accurate and inexpensive analysis methods. Document 1 (the present part of the report) has described the available techniques for the measurement of compounds relevant in gasification of biomass and waste, including tar, particles, and gaseous gas contaminants. Moreover, examples of implementation of gas analysis in pilot- and commercial gasification plants, and of current joint research efforts, have also been compiled. This report is complemented with a book of factsheets which cover the main analysis methods applied in gasification (see Document 2), and with a collection of video blogs that further illustrate how these techniques are applied in practice (IEA Bioenergy Task 33 Youtube channel).

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