Sampling and analysis of tar and particles in biomass producer gases
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Technical Report

Prepared under

CEN BT/TF 143 "Organic contaminants ("tar") in biomass producer gases"

Date: July 2005

By:

J. Good, Verenum (Switzerland)

L. Ventress, Casella Group (UK)

H. Knoef , Biomass Technology Group, BTG (The Netherlands)

U. Zielke and P. Lyck Hansen, Danish Technological Institute, DTI (Denmark)

W. van de Kamp, P. de Wild, B. Coda, S. van Paasen and J. Kiel Energy research Centre of the Netherlands, ECN (The Netherlands)

K. Sjöström and T. Liliedahl, Royal Institute of Technology, KTH (Sweden)

Ch. Unger, Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT (Germany)

J. Neeft, SenterNovem (The Netherlands)

M. Suomalainen, P. Simell, VTT Processes (Finland)

Table of Contents

1. Aim of the Technical Report

The Technical Report aims to provide background information in support of the CEN Technical Specification "*Biomass Gasification – Tar and Particles in Producer Gases – Sampling and Analysis*" which is being prepared by CEN task force BT/TF 143 WI CSC 03002.4TC. The report is not part of the Technical Specification itself, and the information contained herein is provided for guidance only.

The content of this report is based on the "Tar Guideline", which is a method for sampling and analysis of tars and particles from biomass producer gases, developed in a project under the EU fifth framework programme from 2000 to 2002. When this Guideline was transferred to a CEN Technical Specification between 2003 - 2005, some parts of the technical descriptions were removed as they were examples and not mandatory procedures.

It is the aim of this report to ensure that these technical descriptions remain available as background information for those who work with the Technical Specification.

Definitions, for instance for "tar" and "gravimetric tar" are given in the Technical Specification.

2. Measuring Principle

2.1. Overview

The required level of information about the gasification products often depends on the end use of the gas. In some applications a very rough estimate of the gas heating value is sufficient for successful operation while very detailed chemical characterisation of the effluents may be needed in another application.

The measurement principle is described in this chapter. The principle is based on the discontinuous sampling of a gas stream containing particles and organic compounds (tar) under isokinetic conditions. The instructions for isokinetic sampling of flue gases are given in the standards ISO 9096 or VDI 2066.

The aim has been to keep the principle as simple as possible. This is because the measuring conditions can vary from 'comfortable' laboratory situations to a fullscale operating plant gasifier where there is no customised area for measurements or measurement apparatus. The weather conditions can also be challenging, for instance in northern Europe measurements may have to be performed at temperatures below 0°C.

The tar and particle sampling system consists of a heated probe, a heated particle filter, a condenser and a series of impinger bottles or alternative equipment[1] containing a solvent for tar absorption. The impinger bottles or alternative equipment[1] collecting tar are placed in a temperature controlled bath so that staged warming and cooling of the sampled gas takes place. The gas is sampled for a specified period through the sampling line and filter. The flow rate is maintained with the aid of either process pressure or a pump.

The sampling lines including the filter are heated to prevent tar condensation. However, to avoid thermal decomposition of organic compounds, these temperatures must be properly selected. The actual temperatures are given in the Technical Specification.

The tar collection occurs both by condensation and absorption in isopropanol, which was found to be the most suitable solvent. The volume, temperature, pressure, and gas flow rate through the equipment are measured. The gases from by-pass lines and sample gas are vented safely to atmosphere.

Immediately after sampling the content of the impinger bottles or alternative equipment[1] is decanted into a dark storage bottle, (if a dark bottle is not available, the bottled sample must therefore be stored in a dark place). All surfaces (including metal surfaces) contacting the gas, at temperatures lower than the process temperature, are washed with the solvent. The washes are combined with the actual sample. This is easy to arrange in atmospheric processes, but very difficult in pressurised systems. The storage bottle is stored, tightly closed at a cool (< 5°C) temperature for later analysis.

In general, sampling of tar and particles is performed simultaneously except for pressurised and/or large-scale gasifiers (>20 MW_{th}) where a sampling strategy based on separate sampling of tar and particles is applied. In pressurised processes, isokinetic operating conditions would require much higher sampling flow rates when using the minimal nozzle diameter of 4mm. Hence tar sampling is performed non-isokinetically for pressurised gases. Non-isokinetic tar sampling is also practical in large-scale atmospheric gasifiers where the pipe diameter is large.

Isokinetic sampling is also not required when only tar (and not particles) is sampled and the gas temperature under study at the sampling site exceeds 350°C. Such temperatures generally avoid tar condensation in the form of aerosols and/or droplets and also minimise adsorption of organic species onto particles.

The measuring principle is based upon a modular sample train consisting of a heated probe, a heated particle filter, a condenser, a series of impinger bottles or alternative equipment[1] containing a solvent for tar absorption, and equipment for pressure and flow rate adjustment and measurement. More details on the sampling train can be found in the Technical Specification. A detailed description of each of the modules is given on the following pages.

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[1]: The alternative equipment is called the "Petersen column". It is described in paragraph 2.4.2.

2.2. Description of sampling module 1 (gas preconditioning)

2.2.1. General

The sampling line consists of a sampling probe, a sampling port (through which the probe is mounted) and additional heated tubes and valves. The line should be short, small in volume and as simple as possible. Additional joints, valves, filters, etc. should be avoided to minimise the risk of leaks. When designing the sampling line consideration should be given to cleaning of the line, sufficient cleaning of sample gas and prevention of condensation.

2.2.2. Isokinetic or non-isokinetic sampling?

For high-temperature (>350°C) sampling, where the tar is completely in gas phase, non-isokinetic sampling is sufficient for measuring tar. In non-isokinetic sampling the alignment of the probe in relation to the gas flow as well as the shape of the probe nozzle can be designed more freely to prevent the nozzle from blocking. This is important especially during pressurised operation since the probe cannot be removed from the gas line. The end of the probe must point against the direction of the gas stream. The tip of the nozzle can be straight-ended or at 45° angled.

Isokinetic sampling requires a special probe. The design of such a probe is described in Paragraph 3.3.

2.2.3. Gas preconditioning for atmospheric gasifiers
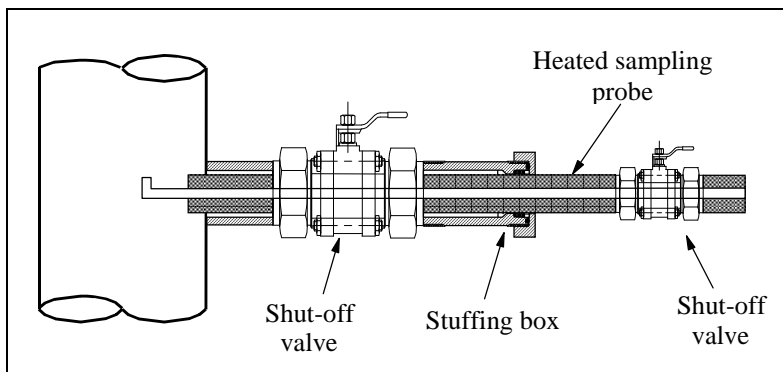
Figure 2-1:   Sampling line for gases containing solid and gaseous
              impurities at atmospheric pressure.

The sampling line under atmospheric conditions is designed in such a way that the probe can be removed through the shut-off valve (ball valve) during operation of the gasifier. The design of the stuffing box is described in more detail in Paragraph 5.2 and Figure 5-2. A second shut-off valve (ball valve) is mounted between the probe and the particle filter for shutting off the sampling line at any time (also in case of leaks). The valve should be resistant to process temperature (high temperature shut-off valve). External heating of the sampling line (for example electrical or hot N_2 circulation in a jacket) prevents condensation of water vapour and condensable gases (clogging of the sampling line). The insulating material should completely cover the sampling line and particle filter to sustain the minimum necessary temperature level and to avoid the formation of cold spots (possible tar condensation) in the line or in the filter.

When only tar is measured, the particle removal from the sample gas can be carried out at the process temperature with a ceramic filter positioned at the tip of the probe (SiC is a suitable material, since it has very little or no catalytic effects on tar decomposition).

The pressure and temperature of gas is measured at the sampling point.

The sampling line for an atmospheric process is shown in Figure 2-1 above.

2.2.4. Gas preconditioning for pressurised gasifiers

For pressurised gases a sampling strategy with separate sampling of tar and particles is required. The gas preconditioning is composed of an inline ceramic filter for the particle collection followed by a pressure relief device (Figure 2-2). The whole sampling line is heated and tar is sampled at ambient pressure.
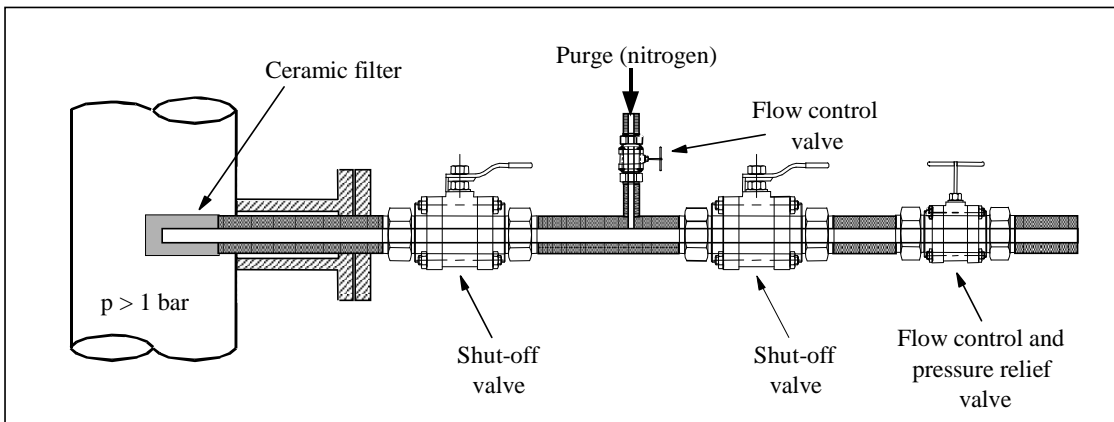
Figure 2-2:   An example of a sampling line for a pressurised process for tar measurement only

A shut-off valve is positioned first in the sampling line enabling shut off at any time (also in case of leaks). The shut-off valves must endure the gas temperature at the process pressure. The material of the valves must be carefully selected for each process.

Pressure relief is carried out in stages with three manual control valves. It can also be performed with one valve only (flow control), but steadier pressure relief and increased reliability (leaks due to contamination of valves) are achieved by installing several valves. Pressure relief and clogging in the sampling line are monitored by pressure measurements.

The last valve (flow control and pressure relief valve) in the line, from which the gas is led through a PTFE hose or glass pipe into the condenser, regulates the flow of sample gas. The length of this line should be kept to a minimum.

Condensation of water vapour and condensable gases before the condenser is prevented by heating the sampling line (for example electrically or by hot N_2 circulation). This prevents blocking of the sampling line. Blocking problems can also be minimised by using two parallel sampling lines equipped with facilities for purging and solvent washing. The type and number of particle separators in the sampling line is chosen on the basis of solids contents in the sample gas. Both quartz and fibreglass filters can be used as hot filters while, when measuring tar only, ceramic filters can be employed.

As it is not possible to remove the probe from the sample port under pressurised conditions, the sampling probe and the filters can be cleaned by nitrogen purge. Nitrogen flush lines are positioned to ensure that the most important valves and gas lines are cleaned in both directions.

The nitrogen flush of the probe tip has to be continuous except during the sampling.

2.3.   Description of sampling module 2 (particle filter)

Particles are collected in an external heated filter system. Quartz filters (absolute filters) should be used as filter material. Retention capacity of the filters should be at least 99,998 % of the particles of size 0,3 μm (DOP standard[2]).

For particle concentrations above 20 mg/m$_n$^{3}, thimble filters are used. Dimensions of thimble filters are selected for subsequent Soxhlet extraction procedures. The recommended dimensions for the thimble filter are a

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[2]: The test method was developed in USA during World War II. DOP is Bis(2-ethylhexyl) Phthalate and is (like other Phthalates) an undesirable compound according to National and EU environmental rules. The most common test aerosols nowadays are Latex particles or DEHS Di (2-ethylhexyl) Sebacate or DOS Dioctyl Sebacate. The term 'DOP test' is used in everyday language, but DOP is not used any more.

diameter of 30 mm and a length of 77 or 100 mm. As a general indication, a filter surface area of 100 cm^2 allows the collection of several grams of particles without significant increase in pressure drop over the filter.

The filter holder must be gas tight. An example of a possible way to mount the filter is shown in Figure 2-3.
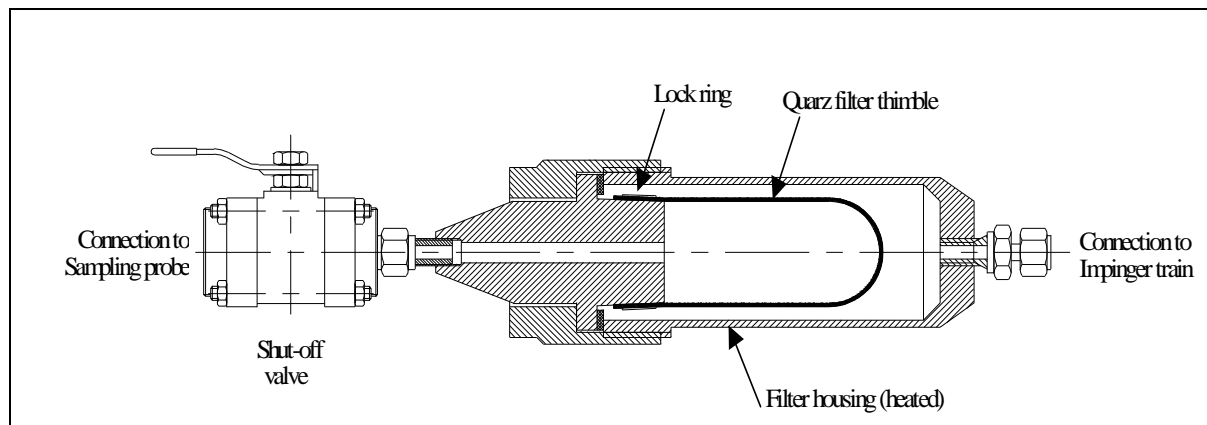

Figure 2-3: Module 2: the heated particle filter. This figure shows one of the possible ways to mount the thimble filter in the housing.

The material of the filter holder should not affect the composition of tar compounds and must endure 50°C higher temperature than the operating temperature (e.g. AISI 310, AISI 316). A thermocouple is placed inside the filter holder to measure the gas temperature at the filter.

The temperature of the filter is critical. It must be sufficiently high in order to prevent filter plugging, caused by the tar build-up, but low enough to prevent further reactions of tar on the filter surface. Temperatures are given in the Technical Specification.

In case of non-isokinetic tar sampling applications, the particle removal from the sample gas can be undertaken with a ceramic filter at the process temperature, which is positioned at the tip of the probe. SiC is a suitable material for this filter as SiC has very little or no catalytic effects on tar decomposition. Reverse flow, high-pressure nitrogen purge should be available to clean the particles from the SiC filter.

2.4. Description of sampling module 3 (tar collection)

The connection between the hot metal tubing and the glassware must be carefully designed to assure the tightness of the joint. One possible design principle is as follows: The end of the metal tubing is formed to be identical to the male glass ball ground joint so that it fits the female ground joint of the impinger bottle. The radius of the metal ground joint should be the same, or slightly smaller, than the glass joint. The smaller radius makes the cracking of the female glass joint due to different thermal expansion less likely, however special attention then needs to be given to the sealing of the joint.

Collection of moisture and tar is performed in a series of 6 impinger bottles or in a specially designed equipment referred to as "Petersen column". The sampling principle and equipment of these two equipments (6 impinger bottles and Petersen column) are described in paragraph 2.4.1 and paragraph 2.4.2, respectively.

2.4.1. Series of impinger bottles

A schematic drawing of the impinger bottles is shown in Figure 2-4.

In the series of impinger bottles, the first impinger bottle acts as a moisture collector, in which water and tar are condensed from the process gas by absorption in isopropanol. The heat released by gas cooling and condensation is removed either in an external water bath or by an additional heat exchanger before the condenser. The heat exchanger may be necessary for high moisture producer gases (e.g. from steam gasification) and should be designed to meet the demands of the gasifier.

The condenser is a standard impinger bottle (reference arrangement) or can optionally be equipped with an internal liquid quench system which is especially suitable for producer gases containing higher tar levels. When using a liquid quench, isopropanol is the circulating liquid. The working principle of the liquid quench is described in Appendix 9.1.
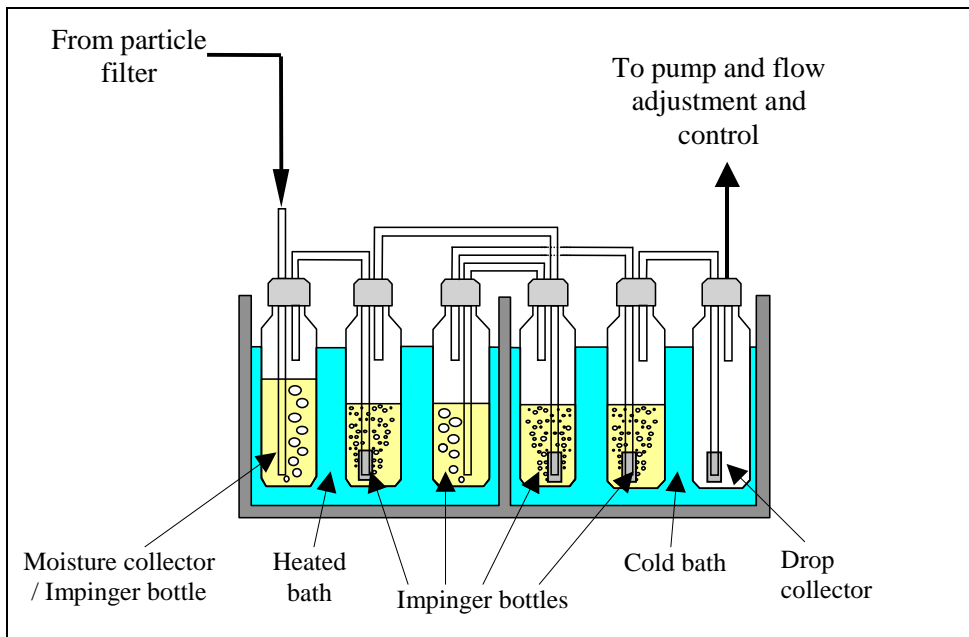
Figure 2-4: Example of module 3 of the sampling train: Impinger bottles

There are two possible impinger set-ups, which are described in more detail in the Technical Specification. A brief description of the sampling principle and equipment is given here.

After the moisture collector the gas is passed through a series of 4 impingers with solvent and 1 final impinger which is empty. Direct condensation of the liquid effluent without diluting media, e.g., with cold trapping, can result in further reactions of the trapped compounds.

Fine-meshed frits give better results than coarse-meshed frits; G3 frits should be installed in the impinger train. If G3 frits give a too high a pressure drop (e.g. 0,5 bar), G2 frits should be used.

Standard glass impingers (100 ml or 250 ml volume) with an inner tube diameter of 4 mm are recommended. An alternative modified impinger design is shown in Appendix 9.2.

Cooling liquid can be either made of a mixture of salt/ice/water or a mixture of dry ice with isopropanol or by a mechanical cooling device. The bath should be insulated.

2.4.2. Petersen column

DTI has developed an alternative equipment for the 6 impinger bottles in module 3. The name of this alternative equipment is ”Petersen column” after the inventor Finn Petersen. The "Petersen column" consists of two washing stages filled with isopropanol. Stage 1 is a traditional washing stage with an impinger. The bottom of stage 2 consists of a G3 glass frit with two functions: a) it retains tar droplets (aerosol) and b) it generates a large number of very small gas bubbles in washing stage 2 which results in an improved washing efficiency. The two washing stages are filled with the washing medium (solvent, isopropanol) through two nozzles. During normal pressure (atmospheric pressure), the solvent is kept back in stage 2 by the glass frit, as the liquid runs very slowly through the frit. If there is a little vacuum in washing stage 2, no liquid runs through the frit.

Figure 2-5 shows the "Petersen column". A more detailed description plus the requirements for the essential dimensions are given in the Technical Specification.

The "Petersen column" is jacket cooled. The cooling fluid and cooling temperature can be selected as required e.g. in relation to the gas temperature. The column is constructed in such a way so it is easy to replace the glass frit if it is polluted by particles that cannot immediately be rinsed out with solvent.

When sampling has ended, the tube which is connected to the vacuum pump is moved to the connecting stub at the drain cock at the bottom of the "Petersen column". By creating a little vacuum in washing stage 1, the solvent is sucked from washing stage 2 through the frit. That results in washing stage 2 being emptied at the same time as the frit is cleaned by the solvent. Solvent from both washing stages is collected in a storage bottle which is kept sealed against the cone of the drain cock.

Tests have shown that the "Petersen column" has a high sampling efficiency. During measurements in heavily polluted countercurrent gas, less than 1% of the chromatographable tar is found in a backup system. 85% of this material consists of benzene.
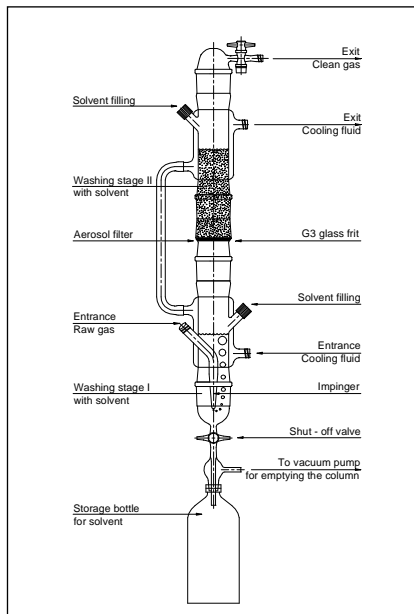
Figure 2-5: The "Petersen column"

2.5. Description of sampling Module 4 (volume metering)

Figure 2-6 displays the Module 4 equipment: a pump, a flow control valve, a flow indicator, pressure and temperature measurement and a volume flow meter.

2.5.1. Sample gas suction device

The gas suction pump (vacuum pump) must be oil free, airtight and pulsation must be minimal. Membrane pumps are recommended because of easy clean up and maintenance. The gas pump must be able to displace at least $1m^3_n$/h at an absolute pressure of 50000Pa. A flow control valve is recommended to adjust the sample flow rate.

There is no need for a pump when sampling pressurised gasification systems at pressures much larger than 10^5Pa. However, for gasification systems which are only slightly over-pressurised, (up to 150kPa), a pump may still be needed.
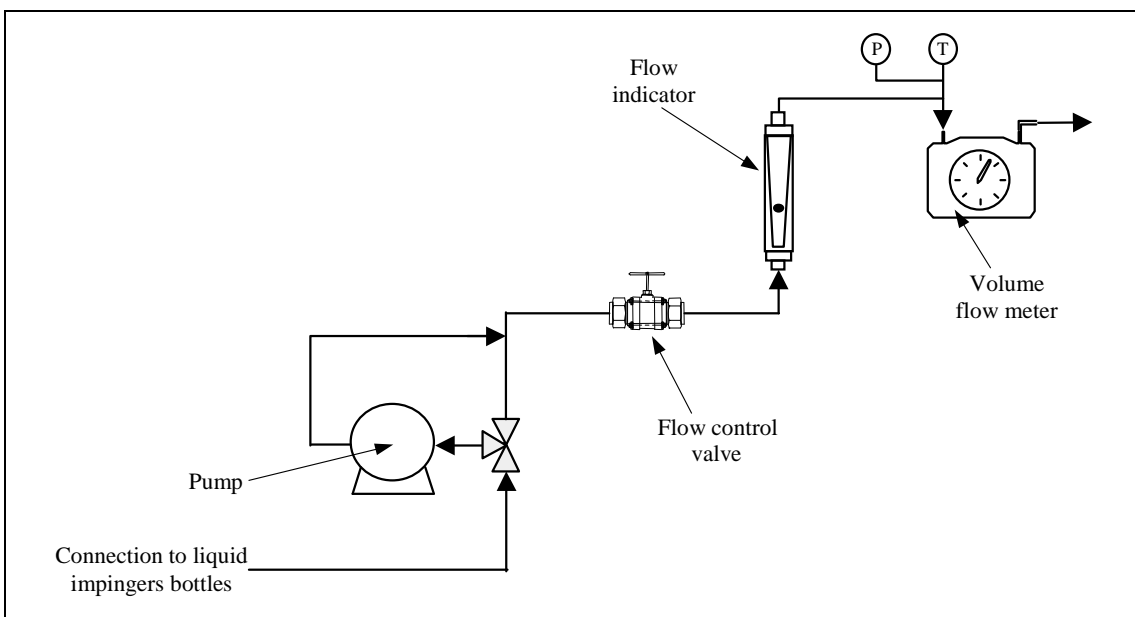
Figure 2-6:   Pump and flow measuring equipment in Module 4.

2.5.2. Sample gas meter

To determine the volume of sampled gas, a barometer and a calibrated dry gas meter with thermocouple and indicator for pressure difference are used. The pressure drop over the volume-measuring device should not exceed a few hundred Pa.

The gas flow during the removal of flushing gases and essential sampling is monitored with a rotameter. The rotameter should be located between the pump and the volume-measuring device, which is used to adjust and compensate the sample flow. A temperature indicator, differential pressure indicator and a barometer are used to correct for temperature and ambient pressure to normal conditions.

The exhaust gases from by-pass lines and sample gas must be safely vented to atmosphere.

2.6. Equipment and materials

For sampling line temperatures below 200°C, PTFE or glass tubing is used. For higher temperatures up to 700°C, stainless steel tube (AISI 316 or AISI 310) is a suitable material.

When the temperature exceeds 700°C the accumulation of the catalytically active matter (for example limestone or dolomite) to the tip and bends of the probe may prove problematic.

The equipment and materials required for the construction of sampling system are presented in Table 2-1. All materials and equipment used in sampling should be compatible with national safety regulations. In case the sampling environment is classified as potential explosion area (e.g. standard EN 60079-10) electrical equipment used in sampling should fullfill the required national safety regulation for potentially explosive atmospheres (e.g. standard EN-50014).

Table 2-1:   Materials and equipment for sampling system.

Probe :	Acid-proof stainless steel, AISI 316 or Fire-proof stainless steel, AISI 310
Condenser:	Acid-proof steel, AISI 316, glass
Filter:	Quartz fibre filter, size 30 x 77mm
	Max. temperature 950°C
	Retention capacity 99.998% (0.3 μm), DOP-stand.
Filtration:	Filter holder: Acid-proof steel, AISI 316
Ceramic filter:	Silicon carbide, 50 x 30 x 135 mm
	Silicon carbide, o.d. 12.7 mm, i.d. 20.5 mm, length 100 - 300 mm
Liquid quench:	Peristaltic pump (3 l/h; 3 m riser level) with Tygon tube, PTFE and stainless steel tubing
Pumps (e.g.):	Membrane pump
Rotameters (e.g.):	Standard rotameter for gas flow rates 1 - 20 l/min
Gas meter:	Dry gas meter
Impinger bottles:	Material is standard laboratory glass (100 ml or 250 ml)
Glass beads:	o.d. 6 mm
Solvent:	Isopropanol, minimum purity 99%. The solvent should not include GC detectable amounts of relevant tar compounds (blank determination by GC essential).
Cold bath:	Acid-proof steel, AISI 316
	Ice bath with salt, ice
	Compression cooler
Sample bottles:	500 ml glass storage bottle with PTFE coated screw plug (GL45) and pouring ring
Gaskets in the filter holder etc.	PTFE or graphite or copper or Viton

3. Isokinetic sampling

3.1. Introduction

Isokinetic sampling means that the velocity entering the sample probe (nozzle) must equal the free stream velocity of the gas being sampled:

$$v'_a = v'_N \qquad \text{(Eq. 3-1)}$$

When the sample gas velocity v'_N is higher than the gas velocity in the duct v'_a, the sampling is designated as over isokinetic. Since over isokinetic sampling implies lower sampling errors in particle concentrations and exact isokinetic sampling is not always possible in practice, the sampling should be conducted within the following limits:

$$0.95 < \frac{v'_N}{v'_a} < 1.15 \qquad \text{(Eq. 3-2)}$$

Within this Technical Report, two isokinetic sampling principles and one quasi-isokinetic principle based on a mass balance are described. The principles are:

a) Measurement of dynamic pressure with a pitot tube followed by determination of actual gas velocity and isokinetic flow rates

b) Measurement of static pressure difference with an O-type probe and adjustment of isokinetic sampling conditions

c) Estimation of the producer gas generation rate by applying a mass balance

3.2. Adjustment of isokinetic sampling based on pitot tube measurement

Pitot tubes measure the pressure difference between the total pressure and the static pressure = the dynamic pressure in the sampling line. When using a standard pitot tube, the gas velocity v'_a at a sampling point is expressed as

$$v'_a = \sqrt{\frac{2 \cdot \Delta p_{Pt}}{\rho'_a}} = \frac{q'_{Va}}{A \cdot 3600} \qquad \text{(Eq. 3-3)}$$

In connection with this Technical Report the dried gas sample flow rate q_{Vg} is measured by a gas volume meter. The velocity in the nozzle opening amounts to

$$v'_N = \frac{q'_{VN}}{a \cdot 3600} = \frac{q_{Vg}}{a \cdot 3600} \cdot \frac{p_{am} + p_g}{p_{am} + p_a} \cdot \frac{273.15 + \Theta_a}{273.15 + \Theta_g} \cdot \left(1 + \frac{f_n}{0.804}\right) \qquad \text{(Eq. 3-4)}$$

From equations 4-1, 4-3 and 4-4 it follows that the volumetric gas flow rate through the gas meter becomes

$$q_{Vg} = \sqrt{\Delta p_{Pt}} \cdot 3600\, a \cdot \sqrt{\frac{2}{\rho'_a}} \cdot \frac{p_{am} + p_a}{p_{am} + p_g} \cdot \frac{273.15 + \Theta_g}{273.15 + \Theta_a} \cdot \frac{1}{(1 + \frac{f_n}{0.804})} \qquad \text{(Eq. 3-5)}$$

A list of symbols is given at the end of this chapter.

3.3. Adjustment of isokinetic sampling conditions using O-type probe

Isokinetic sampling is best performed using an O-type probe, which incorporates separated hollow chambers surrounding the nozzle. The hollow chambers (measurement chambers) are provided with a number of holes internally and externally, which connect the chambers with the interior and the exterior of the nozzle through which the main stream of gases pass. The static pressure in the chambers is monitored via pipe connections to the pressure gauge. Figure 3-2 shows an O-type nozzle of this design, however, it has the disadvantage that special fabrication is required. A simpler O-type probe is illustrated in Figure 3-1.
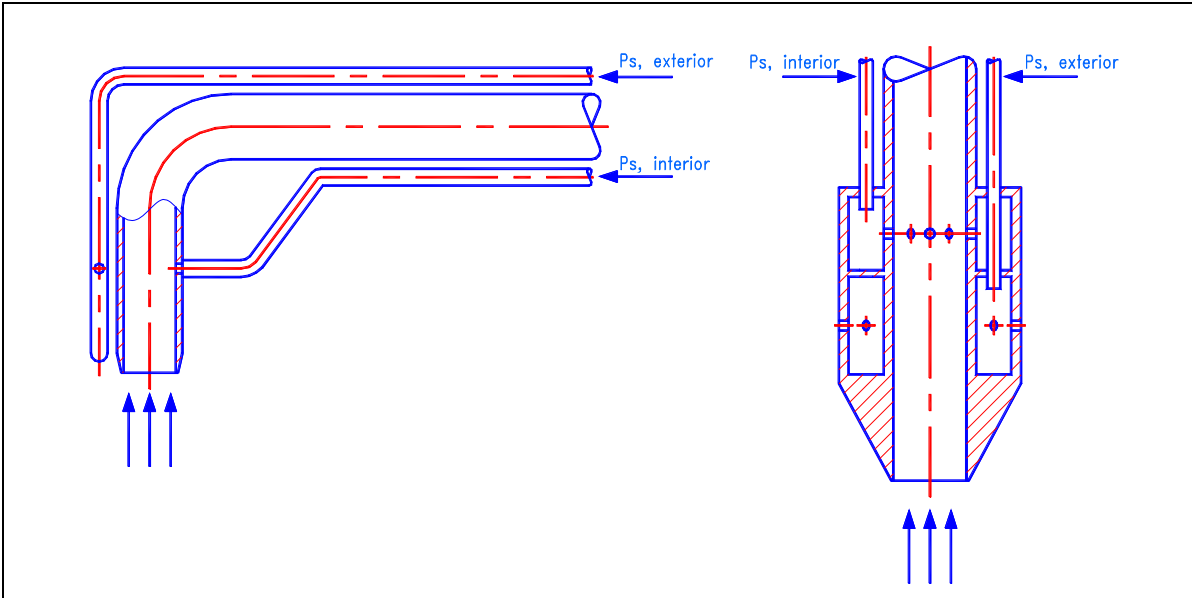
Figure 3-1   Simple O-type probe   Figure 3-2   O-type probe

An O-type probe configuration for isokinetic sampling can be used both for sampling atmospheric pressure gas and pressurised gases. For sampling from pressurised systems an O-type probe configuration is the preferred choice; this type of probe has been found to operate relatively well under pressure.

Isokinetic sampling conditions are achieved by equalising the interior and exterior static pressure signal. Figure 3-3 shows how the pressure difference is measured. When the difference between the two signals is zero, the gas velocity in the nozzle is deemed to be the same as outside the nozzle. Continuous equalisation is established by means of the bypass valve on the vacuum pump.
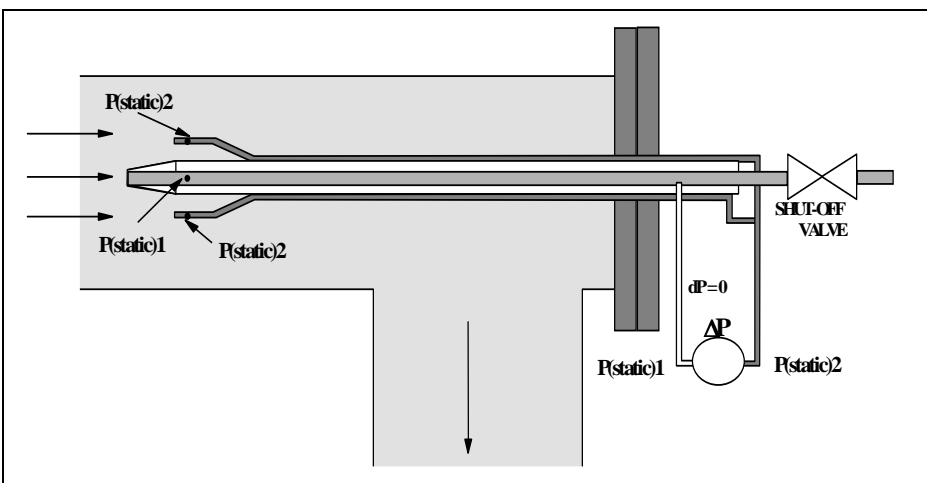
Figure 3-3   The configuration of the O-type probe

A series of tests have been carried out in order to determine the magnitude of errors resulting from deviations from the zero pressure. The tests show that in low velocity streams significant sampling errors may result from small deviations from zero pressure. For example, in a duct with a gas velocity of 5m/s, a 40% sampling error may result from a 12 Pa deviation from zero. For a gas velocity of 15m/s, the same deviation from zero would result in only a 3% sampling error. In sites where steady flow conditions frequently do not exist and in low velocity streams the use of O-type probe is not reliable and it is useful only as a rough means of adjustment to approximate isokinetic conditions.

Isokinetic sampling is required for particles and low-temperature tar sampling points (temperatures under 350°C), where a proportion of the tar can be present as aerosols in the gas. In the case of isokinetic measurements the number of measuring points is defined by the diameter of the gas pipe. Details are found in ISO 9096 or VDI 2066. For non-isokinetic sampling one measurement point is sufficient.

3.4. Calculation of isokinetic sampling conditions

Where pitot tubes or O-type probes cannot be used or are not available, the producer gas flow rate and the isokinetic sampling flow rate can be calculated from a nitrogen based or carbon based mass balance. The nitrogen based mass balance can be applied to air-blown gasifiers, the carbon based mass balance can be applied to all types of gasifiers (air-blown, oxygen- and oxygen/steam gasifiers. In case of gasification systems with two resulting gas streams (like the Güssing gasifier or the Ferco Silva Gas gasifier), two mass balances are needed to calculate the producer and the exhaust gas yields.

The nitrogen based method provides the actual producer gas flow rate (m^3_n: normal conditions, 273,15 K, 101325 Pa = 1,01325 bar, dry basis). As the sampled gas volume is also measured as dry gas, the target isokinetic sampling flow can be controlled during sampling by monitoring and adjusting the gas meter.

The nitrogen content in the producer gas can be measured directly (GC based measurement) or as the difference of 100% of all other main producer gas components (CO, CO_2, CH_4, H_2, H_2O).

$$q_{V,producer\,gas} = q_{V,air} \cdot \frac{N_{2,air}}{N_{2,producer\,gas}} \qquad \text{(Eq. 3-6)}$$

where $q_{V,producer\,gas}$ = Producer gas flow rate [m^3_n/h]

$q_{V,air}$ = Primary air flow rate (gasification agent flow rate) [m^3_n/h]

$N_{2,air}$ = N_2 content of primary air (gasification agent) [Vol.-%]

$N_{2,producer\,gas}$ = N_2 content of primary air (gasification agent) [Vol.-%]

The carbon based method presented here is based on a total carbon balance and can be applied when the following requirements are satisfied:
a) Gasifier operation is stable;
b) Main gas composition (CO, CO_2, CH_4) is known;
c) Fuel feeding rate (in kg/h), fuel moisture and carbon content are known;
d) Solid or liquid carbonaceous effluent streams (bottom ashes, particles, tar) and their carbon content are known.

The general calculation of the producer gas flow rate based on an elemental carbon balance can be written as

$$q_{m,\,fuel}cc_{fuel} + \sum q_{V,agent}cc_{agent} = q_{V,gas} \cdot \left(cc_{gas} + c_{tar}cc_{tar} + c_{particles}cc_{particles} \right) + q_{m,ash}cc_{ash} \quad \text{(Eq. 3-7)}$$

where $q_{m,\,fuel}$ = Fuel feeding rate [kg dry biomass / h]

cc_{fuel} = Carbon content of fuel [kg C / kg dry biomass] (= 0.47 for woody biomass)

$q_{V,agent}$ = Gasification agent feeding rate [m^3_n/h]

cc_{agent}	=	Carbon content of gasification agent [kg C / m^3_n]
$q_{V,gas}$	=	Producer gas generation rate [m^3_n/h]
cc_{gas}	=	Carbon content of non-condensable gases (CO, CO_2, CH_4) in producer gas [kg C / m^3_n]
c_{tar}	=	Tar concentration in producer gas [kg/m^3_n]
cc_{tar}	=	Carbon content of tar [kg C / kg tar]
$c_{particles}$	=	Particle concentration in producer gas [kg/m^3_n]
$cc_{particles}$	=	Carbon content of particles [kg C / kg dry biomass]
$q_{m,ash}$	=	Bottom ash rate [kg dry ash / h]
cc_{ash}	=	Carbon content of bottom ash [kg C / kg dry ash]

Generally, the gasification agent does not contain carbonaceous gas components, hence cc_{agent} = 0 except, for example, when the bed material contains carbon containing additives like limestone. Dividing equation (Eq. 3-7) by the fuel feeding rate and rearrangement gives the specific producer gas yield

$$Y_{gas} = \frac{q_{V,gas}}{q_{m,fuel}} = \frac{cc_{fuel} - c_{ash,fuel}\ cc_{ash}}{cc_{gas} + c_{tar}\ cc_{tar} + c_{particles}\ cc_{particles}} \qquad \text{(Eq. 3-8)}$$

| where | Y_{gas} | = | Producer gas yield [m^3_n/kg dry biomass] |
| | $c_{ash,fuel}$ | = | Ash content of fuel [kg / kg dry biomass] |

The carbon based method determines the producer gas yield on dry basis and does not require any information on the moisture content of the producer gas. Multiplication of the gas yield by the fuel feeding rate (dry basis) provides the actual producer gas flow rate. As the sampled gas volume is also measured as dry gas, the target isokinetic sampling flow can be controlled during sampling by monitoring and adjusting the gas meter.

Analogous to the pitot tube velocity measurement, the calculation of the effective isokinetic sampling conditions from equation (Eq. 3-8) can also be performed after the sampling.

The producer gas yield is a characteristic feature of the chosen gasification reactor under the given operating conditions (load, fuel moisture, fuel type etc.). Examples of producer gas yields are given in Table 3-1.

For a typical co-current gasifier, the fraction of carbon found in the bottom ash, particles and tar typically amounts to 1% of the total carbon in the gas. Hence, the carbon in the carbonaceous effluent streams has no significance for the producer gas yield calculation for such type of gasifiers. For counter-current and fluidised-bed gasifiers, the amount of carbon in particles and tar ranges from 10% to 15% of the total carbon in the gas. In these cases, some prior information regarding the tar and particle levels is required to determine gas yields accurately.

Another method for estimation of the producer gas flow rate which can be used, e.g. for co-current gasifiers coupled to IC engines, is based on the determination of the displaced gas volumes within the engine cylinders [Ramackers et al., 1985]. This method requires the cylinder volume, the engine speed and air supply and the oxygen content in the exhaust gas.

		Countercurrent fixed bed gasifier	Cocurrent fixed bed gasifier	CFB gasifier
Fuel moisture	wt% (daf)	50	16	15
Ash content	wt% (daf)	1	1	1
C in bottom ash	wt%	1	50	10
H_2	%	18.0	14.2	14.8
CO_2	%	7.0	12.9	15.0
CO	%	32.0	18.0	15.4
CH_4	%	5.0	1.9	4.2
Particle	mg/m^3_n	200	1,000	20,000
$c_{particles}$	Kg/m^3_n	$2\cdot10^{-4}$	$1\cdot10^{-3}$	$2\cdot10^{-2}$
Tar	mg/m^3_n	100,000	1,000	20,000
c_{tar}	Kg/m^3_n	0.1	$1\cdot10^{-3}$	$2\cdot10^{-2}$
Gas yield Y_{gas} according to Eq. 3-8	m^3_n/kg (daf)	1.84	2.73	2.23
Fraction of C in particles, bottom ash and tar	% of total C in gas	11.3	1.0	15.5

Table 3-1   Calculated producer gas yields from various gasifiers using wood as fuel

Remarks: A survey of typical gas composition, tar and particle concentrations from various gasifier reactor types is given in Appendix 9.3. Carbon content of the fuel is 47 wt% (see previous page) (typical for wood); carbon content in particles, bottom ash and tar are estimated from typical experimental data.

3.5.   Calculation of nozzle diameter

The nozzle diameter is chosen in order to adjust the velocity in the nozzle to the surrounding duct velocity. Furthermore, the correct choice of nozzle contributes to obtain a suitable duration of sampling and a suitable sample flow rate. The suitable sample flow rate through impinger bottles is often a barrier for proper isokinetic sampling. Several CEN standards recommend a flow rate between 8 and 33 l/min for Midget and Greenburg-Smith impingers and a flow rate between 1 and 3l/min for impinger bottles with frits. A specially designed VTT impinger is suitable for the range of 2 to 10l/min.

With a maximum flow rate of 10 l/min and a minimum nozzle diameter of 5mm it is possible to make isokinetic samplings up to a maximum gas velocity of 8.5m/s on the condition that there are constant gas conditions through the sampling train. As producer gas normally contains some moisture and has a higher temperature than the gas in the sampling train, the velocity will be higher than 8.5m/s in practice.

A general expression for calculation of nozzle diameter based on known gas velocity (measurement with pitot tube including moisture content) can be derived from the following equations:

$$v'_N \cdot a \cdot 3600 \quad = \quad q'_{VN} \quad = \quad q_{Vg}\,(1+\frac{f_n}{0.804})\cdot\frac{p_{am}+p_g}{p_{am}+p_a}\cdot\frac{273.15+\Theta_a}{273.15+\Theta_g} \qquad \text{(Eq. 3-9)}$$

where the nozzle face area a:

$$a \quad = \quad A\cdot\frac{q_{Vg}}{q'_{Va}}\,(1+\frac{f_n}{0.804})\cdot\frac{p_{am}+p_g}{p_{am}+p_a}\cdot\frac{273.15+\Theta_a}{273.15+\Theta_g} \qquad \text{(Eq. 3-10)}$$

where $0.1 \leq q_{Vg} \leq 0.6$ m³ₙ/h and the nozzle diameter d_N is calculated as follows:

$$d_N = \sqrt{\frac{4 \cdot a}{\pi}}$$
(Eq. 3-11)

A general expression for calculation of nozzle diameter based on the assumption of a gas yield shown in Table 3-1 appears from the following equation. With a gas yield value from Table 3-1, which fits the present object, it is possible to calculate the wet producer gas flow q'_{Va} and the gas velocity v'_a as follows:

$$q'_{Va} = Y_{gas} \cdot \dot{m}_{fuel} \cdot \frac{101300 \cdot (273.15 + \Theta_a)}{273.15 \cdot (p_{am} + p_a)} \cdot (1 + \frac{f_n}{0.804})$$
(Eq. 3-12)

$$v'_a = \frac{q'_{Va}}{A \cdot 3600}$$
(Eq. 3-13)

The appropriate nozzle area is expressed by:

$$a = A \cdot \frac{q'_{Vg}}{q'_{Va}} = A \cdot \frac{q_{Vg} \cdot (1 + \frac{f_n}{0.804})}{q'_{Va}} = A \cdot \frac{q_{Vg} \cdot 273.15 \cdot (p_{am} + p_a)}{Y_{gas} \cdot \dot{m}_{fuel} \cdot 101300 \cdot (273.15 + \Theta_a)}$$
(Eq. 3-14)

According to ISO 9096 the minimum nozzle size should be 4 mm.

where
a	=	Nozzle face area [m²]
A	=	Producer gas duct cross section area [m²]
v'_a	=	Wet producer gas velocity in duct [m/s]
v'_N	=	Wet gas velocity in nozzle [m/s]
q'_{Va}	=	Wet producer gas flow through duct [m³/h]
q'_{VN}	=	Wet producer gas flow through nozzle [m³/h]
q_{Vg}	=	Dried volumetric gas flow rate through the gas volume meter [m³ₙ/h]
Δp_{Pt}	=	Pressure difference of pitot tube [Pa]
p_{am}	=	Ambient pressure [Pa]
p_a	=	Static pressure in producer gas duct [Pa]
p_g	=	Static pressure in the gas volume meter [Pa]
Θ_a	=	Temperature in producer gas [°C]
Θ_g	=	Remperature in gas volume meter [°C]
f_n	=	water vapour concentration in dried sample gas [kg/m³ₙ]
ρ'_a	=	Density of wet producer gas [kg/m³]
$\dot{m}_{fuel}$	=	Fuel feeding rate [kg dry biomass / h]
Y_{gas}	=	Producer gas yield [m³ₙ / kg dry biomass]

4. GC analysis to measure tar compounds

4.1. Scope

The method given in this chapter is an example of how to measure tar compounds with GC-FID. The method is an example, meaning that the actual method to be used can be chosen freely as long as the requirements that are given in the Technical Specification are met. These requirements are given in the chapters "Preparation of analysis" and "Analysis procedures" of the Technical specification.

This method is designed for determination of the total GC-tar content (calculated as naphthalene) in isopropanol (2-propanol) samples.

The method may be extended to include additional specific compounds, provided that the method is validated for each individual case.

4.2. Normative references

The following normative document contains provisions, which through reference in this text constitute the provisions of this method.

VDI 2457 part 1 and ISO 11338-2:2003.

4.3. Analysis procedure

In this paragraph, an example of a GC method is given including conditions. Other conditions are possible. The requirements that the GC method should fulfil, are given in the Technical Specification.

4.3.1. Principle

The tar content sampled in iso-propanol is analysed by gas chromatography using a flame ionization detector.

This method includes two different methods for the calibration procedure, by external calibration only and by using an internal standard.

4.3.2. Reagents

4.3.2.1.   Isopropanol, min. 99.5% cas. no. [67-63-0]

4.3.2.2.   Naphthalene [91-20-3]

4.3.2.3.   n-Heptane [142-82-5]

4.3.2.4.   n-Triacontane [638-68-6]

4.3.2.5.   o-Terphenyl [84-15-1]

4.3.2.6.   Hydrogen, min. 4.5

4.3.2.7.   Helium, min. 4.6

4.3.2.8.   Nitrogen, min. 4.8

4.3.2.9.   Synthetic air min 4.0 or purified pressurised air (hydrogen free)

4.3.2.10.   Standard stock solutions

Standard stock solutions are prepared by dissolving pure or - if available - certified reference standards in a suitable solvent.

Unless the manufacturer's information or stability trials indicate otherwise, the solutions should be stored at around +4°C in the dark.

Prior to use, the solutions should be brought to ambient temperature.

4.3.2.11.   Intermediate standard solutions

Prepare intermediate standard solutions by a suitable dilution of the stock solution (3.2.11) with iso-propanol to a concentration of 0.1 mg/ml.

4.3.2.12.   Working standard solution

Prepare at least five different concentrations by suitable dilutions of the intermediate standard solution (3.3.5) with iso-propanol.

The lifetime of these solutions is limited to one week.

4.3.3. Apparatus

4.3.3.1.   Gas chromatograph

The (or A) Gas chromatograph is (or should be) fitted with a capillary column, a flame ionization detector and a data processing system. The stationary phase of the capillary column should be bonded poly(5% diphenyl/95% dimethylsiloxane). The recommended dimensions are an internal diameter of 0.25 to 0.32 mm and a length of 30 to 60 m. It should be noted that this length is suited to the defining of total GC-tar but for determining individual compounds the length may be too short.

The use of an autosampler is strongly recommended, especially when using external calibration, because it reduces the errors caused by injection.

If there is any risk that ferrules may be in contact with the sample gas, ferrules made up of no more than 49% graphite (e.g. 60% polyimide/40% graphite) shall be used at the GC column injection inlet to avoid possible absorption of tar compounds.

4.3.3.2.   Microliter syringes

For injecting samples into the gas chromatograph, for making calibration and internal standard solution.

4.3.3.3.   Miscellaneous glassware

Laboratory glassware can be cleaned according to good laboratory practice, for example by using e.g. a cleaning agent (laboratory detergent), followed by an annealing treatment at 500°C for 2 hours.

The efficiency of the treatment shall be randomly verified experimentally using blank determinations to ensure that no interfering contamination has occurred.

4.3.4. Sample preparation

Until required for laboratory preparation, samples should be stored in sealed containers protected from the light at temperature below $5°C$. Samples shall be extracted within one month after sampling has been completed. In some cases (when oxygenated tars are expected, e.g. in raw gases of updraft gasifiers) it may be necessary to store the solution in a sealed, dark bottle under nitrogen atmosphere

4.3.5. GC analysis

4.3.5.1.   In general

The detection limit depends on the volume injected on column and the detector sensitivity. Other factors influencing on the detection limit are purity of the gases and solvents used.

4.3.5.2.   Sample pretreatment

Prior to analysis, the sample is mixed thoroughly to insure homogeneity. The sample is then transferred into the GC vial and diluted with the internal standard. The concentration of the internal standard should preferably be exactly the same as in the calibration standards, otherwise a correction factor is required when calculating

quantitative results. The dilution can be performed for example by a factor of 1:1 corresponding to a concentration of the internal standard of 12.5µg/ml.

4.3.5.3. Instrument parameters

Typical gas chromatograph parameters are:

- Column temperature program: 50°C for 5 minutes. to 325°C at 8°C/min, stop for 5 minutes.

- Injector: Split, 1:75

- Injector temperature: 275°C

- Detector temperature: 300°C

- Injection volume: 1-2 µl

- Carrier gas: Hydrogen or helium, column pressure adjusted so that the linear velocity of hydrogen is 30 – 55 cm/s and of helium 20-40 cm/s. WARNING: Special caution is required when using hydrogen because of the risk of explosion.

It should be noted that the parameters above may not be suited to the determination of individual compounds

4.4. Calibration

4.4.1. In general

The result of the analysis depends on the response factor of the compound(s) used for calibration. Naphthalene is selected for the external calibration procedure, and o-Terphenyl as the internal standard. If the sample contains significant amounts of oxygenated compounds e.g. phenols or guaiacols, the result generated by this procedure will be too low.

The integration interval is defined by the retention time from the apex of n-Heptane to the apex n-Triacontane. Prior to running the samples and calibration standards, a iso-propanol solution of 10µg/ml n-Heptane and n-Triacontane is analysed.

Two different calibration models are described below. The calibration procedure described under paragraph 4.4.3 is recommended for usage with an internal standard. The use of an internal standard will enhance the reproducibility of the analytical method significantly. Furthermore, the peak from the internal standard can be used as a functionality test for every GC run.

If the sample analysed contains considerably high number of different tar compounds, it can be difficult to recover the peak of the internal standard. In these cases the calibration procedure described under paragraph 4.4.2 can be applied.

4.4.2. Calibration using external standards without internal standards

External calibration standards of naphthalene shall be prepared at a minimum of five concentration levels. One of the calibration standards shall be at a concentration near the quantification limit, and the other concentrations shall correspond to the range of concentrations expected in the samples or shall define the working range in the GC-FID system.

A table of values is drawn up which consists of the masses mj in the standard solutions and of the associated measured values Aj (j = number of value pairs). The calibration line can be determined from these values by linear regression using equation (1):

$$A_{Naphthalene} = k * m_{Naphthalene} + b \qquad\qquad \text{(Eq 4-1)}$$

Where

$A_{Naphthalene}$: Measurement value for naphthalene as a function of m

$m_{Naphthalene}$: Mass of naphthalene in the calibration solution

k : Slope of the calibration line

b : Intercept of the calibration line

The linearity of the calibration function is to be checked and must be better than r2 = 0,995.

4.4.3. Calibration using internal standards (ISTD)

The procedure of the internal standard described in this paragraph is restricted to the addition of o-Terphenyl to all samples and working standard solutions.

Follow a procedure similar to the calibration using external standards (paragraph 4.4.2), except that each sample and working standard solutions are spiked with o-Terphenyl to attain the same end concentration for all working standard solutions, for example 12.5 µg/ml. If the concentration of internal standard is not the same in the sample and calibration standards a correction factor is required when calculating the results.

Use the same solvent composition and internal standard concentration for the working standard solutions and the samples.

To determine the calibration line, a series of measurement values is drawn up. It consists of the ratios of the masses m_j of naphthalene to the mass m_{Is} of the internal standard and also of the ratios of the measured values A_j / A_{Is} of the naphthalene peak to the o-Terphenyl peak. From these pairs of values, the calibration line is determined by linear regression using equation (2):

$$(A_{Naphthalene} / A_{Is}) = k * (m_{Naphthalene} / m_{Is}) + b \qquad\qquad \text{(Eq 4-2)}$$

where

$A_{Naphthalene}$: Measurement value for naphthalene as a function of mNaphthalene
A_{Is} : Measured value for o-Terphenyl as a function of mIs
$m_{Naphthalene}$: Mass of naphthalene in the calibration solution
m_{Is} : Mass of o-Terphenyl
k : Slope of calibration line
b : Intercept of the calibration line

The linearity of the calibration function is to be checked and must be better than r2 = 0,995.

4.5. Calculation

4.5.1. In general

To calculate on the tar content, the following assumption is made: There is a functional relationship defined by the calibration function between the signal obtained for all substances m_{Tot} and the mass injected $m_{Naphthalene}$. The evaluation solves the appropriate calibration function for $m_{Naphthalene}$.

4.5.2. Calculation using the external standards without internal standards according to 4.4.2

If an external standard is used, the evaluation is performed using equation 4-3:

$$m_{Tot} = (A_{Tot} - b) / k \qquad\qquad \text{(Eq 4-3)}$$

m_{Tot} : Total mass of chromatogram between the apex of n-Heptane to the apex n-Triacontane subtracted the internal standard.

A_{Tot} : Total measured value of chromatogram between apex of n-Heptane to the apex n-Triacontane subtracted the internal standard.

B : Intercept of the calibration line

K : Slope of calibration line

4.5.3. Calculation using internal standard ISTD according to 4.4.3

If an internal standard is used, the evaluation is performed using equation 4-4:

$$M_{Tot} = (m_{Is}/k) * ((A_{Tot}/A_{Is}) - b) \qquad\qquad \text{(Eq 4-4)}$$

See equations 4-2 and 4-3 for symbols.

4.6. Results

4.6.1. Summary

When the procedure described is applied, it provides one individual result (the total GC-tar content calculated as naphthalene) for each sample. If more than one analysis is done on each sample the standard deviation of the result is reported.

4.6.2. Expression of results

The tar concentrations shall be reported in micrograms per normal gas cubic meter (normal conditions: 273,15K, 101325Pa = 1,01325bar, dry)

5. Preparation of Sampling Equipment

5.1. Design of the sampling line

The sampling line should be kept as short as possible. To prevent plugging problems, the inside diameter of the sampling line should be at least 3mm. The sample nozzle diameter can be calculated according to paragraph 3.5. The minimal nozzle diameter is 4mm according to ISO 9096 and 5mm according to VDI 2066, part 2. The nozzle diameter should be at least 4mm. Design parameters for nozzle shapes used to isokinetic measurements can be found in ISO 9096 or VDI 2066.

The sample probe is either positioned in the same direction as the flow or at a 90° angle to it. The sample line is heat-traced at a constant temperature over the filter. The probe is maintained above the tar condensing temperature, to prevent any condensation in the probe. The determination of the temperature level depends on the gasification application. Since high temperature gas cools very quickly, tubes made of stainless steel are appropriate. For gas temperatures below 200°C, PTFE or glass tubing can be used. For gas temperatures above 600°C, material such as Inconel is preferred. The temperature of the stainless steel sampling probe (AISI 310, AISI 316) should be kept below 700°C to prevent changes to the concentrations of tar compounds.

Gas contact times with all parts of the sampling line should be minimised.

In atmospheric sampling the sampling probe is cleaned after each sample run either by flushing with nitrogen pulses or by dismantling and cleaning it manually. As it is not possible to dismantle the probe between sample runs in pressurised conditions, the probe and the filters are cleaned by nitrogen purge.

5.1.1. Measurement of actual gas velocity

Isokinetic measurement requires the knowledge of the actual gas velocity at the sample point or the use of an O-type probe (see chapter 3).

Gas velocities in producer gas streams at near ambient pressure should be measured with (calibrated) pitot tubes or can be calculated according to paragraph 3.4. The instructions for using pitot tubes are given in ISO 9096; an example of the layout is given in Figure 5-1. Pitot tubes must be heated to process temperature, back-flushing facilities being advantageous.
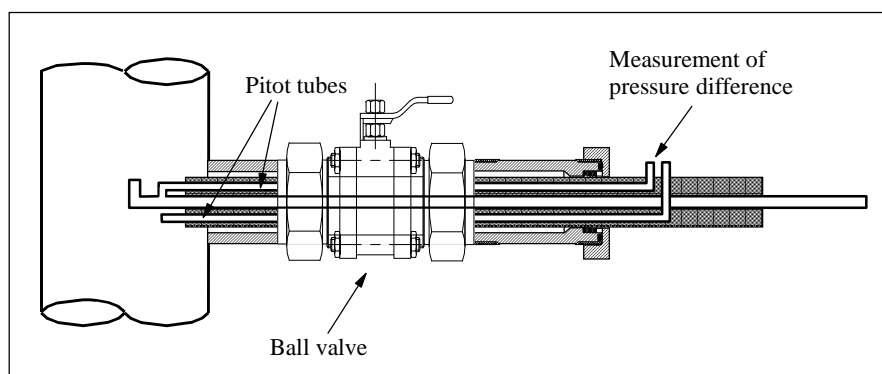
Figure 5-1: Pitot tubes for measurement of the producer gas flow.

In pressurised gasification applications removable pitot tubes cannot be used and hence gas velocities at the probe tip cannot be measured. Alternatively, an O-type probe has been found to work well for pressurised producer gases (Figure 3-3). The O-type probe is also suitable for atmospheric applications.

If there is no velocity meter available calculation is performed according to Paragraph 3.4.

5.2. Design of the sampling port

Sufficient space must be available to ensure easy access to sampling ports and placement of sampling equipment, typically an area of $4m^2$. There should be good ventilation in the sampling site and exhaust gases must be safely vented to atmosphere. Work in the vicinity of pressurised systems should be avoided or kept to a minimum.

In pressurised gasification processes, the O-type probe (Figure 3-3) or other sampling probe(s) must be mounted before the start-up of the plant. The nitrogen flush through the probe tip must be continuous except during the sampling.

In atmospheric processes, probe mounting during operation is possible. The mounting must be carried out safely both for producer gases with positive or negative pressure since combustible and poisonous sample gas exhibits a potential risk of explosion, fire and poisoning.

The joint of the atmospheric sampling probe is illustrated in Figure 5-2. The sampling port includes a main shut-off valve (a 2inch (5,08cm) ball valve) which must be assembled before plant start-up. The sampling probe with the gas tight joint (stuffing box) can be mounted during gasifier operation. The stuffing box structure enables mounting the probe, warming the probe after mounting and displacing the probe without the danger of a gas leak.
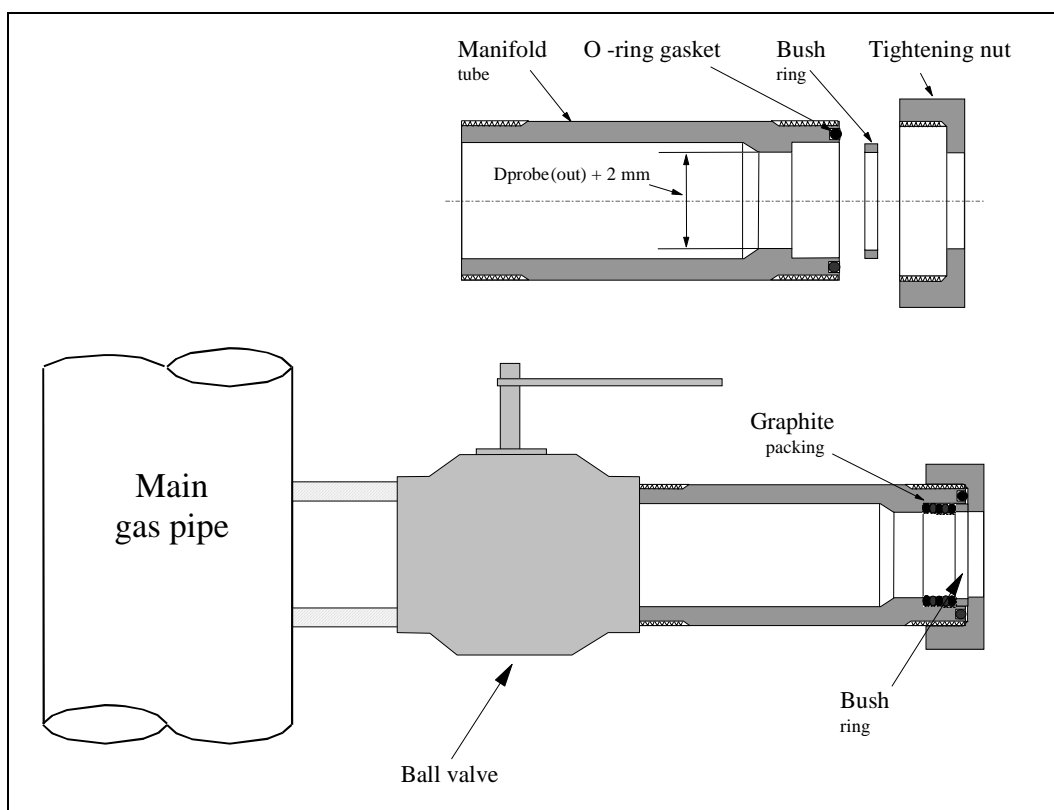
Figure 5-2: Sampling port with lock consisting of a ball valve and stuffing box (the sampling probe is not shown)

5.3. Preparation of the sample train

5.3.1. Gas velocity meter

The pitot tube is the only measurement principle described within this Technical Report which allows a measurement of the absolute gas velocity in the main gas stream. However, its use is limited to gases near atmospheric pressure. Accurate gas velocity measurement requires calibrated pitot tubes. The pitot tubes are

preferentially heated to process temperature. Possible plugging can be tested e.g. by gently blowing nitrogen through the tube. The preparation and calibration instructions of pitot tubes are found in ISO 9096.

5.3.2. Particle filter

Filter thimbles must be preconditioned according to the instructions given in the Technical Specification. A fast, easy and gas-tight clamp system should be used at both ends of the filter holder.

The filter holder including the filter is heated to its set value.

5.3.3. Moisture collector

Prior to sampling the moisture collector cooling or heating system is checked. The preparation procedure depends on the chosen collector system. However, sufficient time should be allowed to ensure that the cooling system reaches the required temperature.

In cases where a liquid quench system is used, the re-circulating system is filled with the chosen liquid. After that, the liquid pump is switched off.

5.3.4. Tar impingers

The required amount of solvent is added to the impingers bottles or to the Petersen column. The impinger bottles or the Petersen column is then heated or cooled to the required temperature. The amount of solvent and the required temperatures are given in the Technical Specification. The impingers bottles or to the Petersen column require approximately 30 minutes to reach the respective heated and cooled bath temperatures.

The cooling liquid can either be a mixture of ice/salt/water or of isopropanol/dry ice or by cryostatic cooling of isopropanol. When using an ice/salt/water cooling mixture operators must ensure that the mixture is wet.

5.3.5. Cleaning of equipment before site measurements

Before using the equipment in connection with a site measurement, all glass equipment shall be cleaned according to an internal laboratory instruction. An example of suitable cleaning procedures is given below. Oil or tar contaminated glass equipment shall be put to soak in an alkaline bath (pH 11-12) for 24 hours. After this the glass parts shall be washed in a laboratory dishwasher with the following program:
- Prewash with softened water
- Mainwash at 85°C or at maximum achievable temperature for 45 minutes
- Rinse 4 times with demineralised water.

After this, the glass parts shall be heated in an oven to 500°C for 2 hours in order to remove possible organic residue on the glass.

After cooling, the glass parts shall be sealed with plastic wrap (parafilm).

PTFE hosing and impinger bottles are rinsed with isopropanol (or with another solvent like DCM and/or acetone to remove yellow-coloured tar residues) under safe laboratory conditions until the tubes appear clean. The cleaning procedure should be regularly checked by analysis of the rinsing liquid. After washing, the tubes are sealed with plastic wrap (parafilm).

5.3.6. Choice of correct nozzle size

The diameter of the sampling nozzle is normally determined by the requirement that the isokinetic sample flow at the beginning of a sample run should equal approximately 70% of the sampling trains pump capacity. In the

Technical Specification the sample flow rate through the impinger bottles is limited to 0.1 - 0.6 m^3_n/h (see also footnote[3]). The calculation of the correct nozzle size can be found in Paragraph 3.5.

5.3.7. Gas suction and volume metering

The calibrated gas volume meter and the pump are connected to the sampling line and to the vent gas line. The temperature and the atmospheric pressure are measured.

5.4. Sampling train leak test

Leaking of the sampling train can be tested either by over-pressurising or evacuating the entire sampling train starting from the particle filter inlet to the gas meter inlet. The test should be done at a pressure, which is 0.2bar above or below the maximum sampling over or under pressure. Step by step instructions for these procedures are given in the Technical Specification.

Pressurising of the train is carried out gently feeding gas from a cylinder into the particle filter inlet and the rest of the sampling train. The exit of the gas pump is locked by a ball valve. The pressure in the sampling line is monitored/observed by a pressure indicator (should stay constant). Possible leaks can also be detected as gas bubbles in the impingers or by using other leak indicators. Carefully opening the shutoff valves after the pump terminates the leakage test. The pressure release procedure must be undertaken with utmost care and should last for at least one minute.

The vacuum leakage test is done by using the gas metering pump. A shut-off valve is placed in a closed position at the inlet of the particle filter. The gas pump is turned on and the pressure is gently reduced to its desired value. Possible leaks are detected as gas bubbles in the impingers or in the Petersen column, or by monitoring the gas meter reading. Termination of the leakage test is performed by carefully opening of the ball valve at the particle filter inlet while the pump is still displacing. When gas bubbles are visible in the solvent, the gas flow rate is reduced by gently opening the bypass valve over the pump. The pressure release procedure must be performed with utmost care and should last for at least one minute.

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[3]: For high gas flow rates, requiring a flow rate through the nozzle higher than 0,6 m^3_n/h to meet isokinetic conditions, this requirement plus the requirement on the minimum nozzle diameter can only be met under isokinetic conditions if the sample flow rate through the nozzle is higher than 0,6 m^3_n/h and if the sample flow is split before the impinger bottles.

6. Reporting and Documentation

6.1. General

Analysis data and results obtained in the laboratory during sampling and at the completion of experimental work are typically recorded and stored in a standardised computer format suitable for easy dissemination. Similarly analysis quality control data should be stored in a suitable master database. Such data typically contain information on gasifier parameters, analysis instrument type and analytical conditions, calibration data including precision and accuracy, etc. Reported analysis values should have been rounded off to its maximum allowed number of significant figures, i.e. the smallest number in any factor.

6.2. Analytical report

Final results of all analyses (particles and tar) are provided in a standard computer file format and forwarded to the requester with cover memorandum. The reports are prepared on the basis of raw data from sampling logs and analysis result files. Examples of sampling logs are given below in Appendix 9.5. The raw log data can be customised to suit a particular report or usage.

Five different numbers are reported with the method for sampling and analysis of tars and particles from biomass producer gases. These five numbers are:

1. The concentration of gravimetric tar in g/m_n^3;

2. The concentrations of individual tar compounds as measured by GC (a suggestive list is given in Appendix 9.4) with a GC retention time of the compounds ranging from benzene to coronene;

3. The sum of concentrations of GC-detected, identified compounds (sum of compounds reported in Annex B of the Technical Specification);

4. The sum of concentrations of GC-detected compounds in the range from and excluding benzene to coronene, calculated as naphthalene (so benzene is excluded from this sum and coronene is included in this sum), given that this concentration can be determined. For the analysis of tars from some gasifier types and/or conditions (e.g. updraft gasifiers, fluidised bed gasifiers operated at 750°C or lower) the number of compounds might be so high that the baseline cannot be properly determined. As this will result in an erroneous amount of GC detected, non-identified compounds, this number will then not be reported;

5. The concentration of particles in mg/m_n^3.

Remarks using suitable designations should be provided with reported data to alert the user to any specific conditions that may have affected the data.

Essential information that should be included in a report may contain the following:
- The name of the laboratory (or factory), from which the sample was received
- The date of sampling and analysis
- Analyst and/or examiner name
- The type of reactor, fuel type, fuel moisture, test number and operation parameters including actual power output (kW), actual fuel feeding rate (kg wet/h), dry raw gas flow rate (m_n^3/h), gasifier start
- Sampling location, i.e. in which part of the reactor the sample was taken
- Sampling technique and essential parameters including tar trapping solvent, ambient temperature and pressure, duct diameter, diameter of sampling nozzle and particle filter temperature
- Sample treatment, solvent, dilution factors etc.
- Sample storage technique
- Analytical technique and parameter settings
- Target analyte values, usually reported in kg/m_n^3 or g/m_n^3
- Level of analytical precision and accuracy

6.3. Sampling log

It is essential to keep records of the principal operating parameters of each gasification run. Examples of typical sampling logs are given in Appendix 9.5.

7. Health and Safety

This section is intended to briefly list potential dangers associated with tar analysis and recommended precautions to avoid exposure to hazardous chemicals and accidents. Take care of the common standards on safety on

- site measurements and procedures
- pre and post sampling, transport, storage and laboratory routines
- special safety measurements for the use of chemicals and laboratory equipment

to be described in the further paragraphs.

For a more comprehensive description of chemical safety issues, the reader should consult the reference sources at the end of the section.

7.1. Introduction

No chemical work is completely risk free but the likelihood of accidents during tar analytical work will be greatly reduced if adequate safety precautions are followed. Health and safety legislation in most countries place duties on employers to ensure health and safety by providing employees with adequate information and training in the inherent hazards of chemical work. Safety issues are usually addressed jointly by supervisors, employees, the local safety representatives and the employer.

7.2. Hazards

Since tar analytical work typically involves handling of relatively small quantities of material the likelihood of acute overexposure to chemical vapour and serious injuries during normal work are less likely. However, acute toxicity hazards may arise during sampling from leaking reactor or sampling system or during sample preparation from spillage and splashes. One should also bear in mind that many sub-operations including operating vacuum devices and handling compressed gases are potentially hazardous and require attention to safety requirements.

General hazards during on site measurement

Before starting measurements on site, the operator has to introduce about the safety measures and actions which have to be considered during the stay at the plant for the preparation of the measurement(s). Discuss the configuration of the sampling equipment and the connection to the plant with the operator + check the compliance with the safety requirements of the sampling with the operator.

Chemical hazards

The use of chemicals is always potentially associated with health, fire and explosion hazards. The health risks associated with accidental exposure to the chemicals being handled depend mainly on their physio-chemical properties, the exposure concentration and exposure time. Toxic body responses can be either reversible or irreversible and response time may be immediate or delayed several days depending on the rates of absorption, bio-transformation, distribution and excretion as well as other factors. Nearly all chemicals found in tar matrices are more or less toxic and for that reason, great care should be exercised in handling samples, solvents and reagents and lengthy exposure above safety limits must be avoided.

The most probable routes to exposure may be through inhalation of non-polar organic solvent vapours since they are the most volatile chemicals. In contrast to water-soluble chemicals and large molecules non-polar solvents diffuse readily through the blood-brain barrier. About 90% of all occupational poisoning are caused by inhalation of non-polar solvents and in particular aromatics and halogenated solvents, which are the most toxic. Solvents can effect the nervous system, the respiratory system, eyes, internal organs including reproductive systems and damage the skin by de-fatting, irritation, sensitisation or dermatitis. Dichloromethane, an often-used tar solvent is a probable human carcinogen and should be handled with great caution and if possible replaced by another safer solvent. For this Technical Specification, 2-Propanol (isopropanol) has been selected

as a less toxic alternative to dichloromethane. Skin absorption is the second route of concern. The rate of skin penetration for solid chemicals is significantly increased if they are dissolved in an organic solvent.

Tar samples can contain many groups of organic compounds depending on the conditions of their formation. The long-term health implications of exposures to such substances are essentially unknown but available literature data that refer to coal-tars present evidence for carcinogenicity to humans. Biomass tars obtained at high temperatures (~900°C) typically contain several of the carcinogenic polycyclic aromatic hydrocarbons (PAH) found in coal tars. Benzene and some of the polyaromatics found in biomass tars have been reported to be carcinogenic for all routes of exposure although skin absorption is the most likely route for PAHs due to their low volatility. Such substances are indirect acting carcinogens and their acute toxicity is generally low. Benzofuran found in low temperature tar is possibly carcinogenic.

Examples of other substances considered most likely to pose a potential risk to human health may be toluene, phenol and its derivatives. The acute toxicity of individual substances may be roughly assessed by comparison with available data (see references). Accordingly, low level exposure to toluene has its primary effect on the CNS and is more acutely toxic than benzene. Phenols are relatively lipophilic and are readily absorbed via the lungs, the digestive organ and skin. Phenol is corrosive to skin, which increase the rate of penetration also for other compounds. It is also toxic to the kidneys and can cause skin allergy, especially following chronic exposure. Many experts consider phenol as a co-carcinogen.

In view of the low volatility and pungent odour of many compounds excessive exposure to vapours does not seem likely unless heating or leakage from the gasifier or sampling system generates fumes. Therefore, the most toxic effects of low volatility substances are expected from dermal exposure. Phenol derivatives, i.e. cresols, xylenols and guaiacyl type phenols are less toxic and corrosive than the mother compound.

Vacuum hazards

Solvents are typically removed under a moderate vacuum of about 1000Pa in a rotary evaporator. Similarly samples are often dried under vacuum in a desiccator.

When working with such devices the operator must be aware of implosion hazards that may result in flying glass and airborne chemicals. Always check for signs of damage (stars or cracks) before use. For greater protection, use a desiccator shield during and after evacuation and wear safety spectacles.

Compressed gas hazards

Compressed gases present potential mechanical and chemical hazards and cylinders and regulators must therefore be handled carefully. Cylinders must always be secured by chains or strong straps to prevent tipping and regulators must always be accessible. Flammable gases must be stored in a well-ventilated area and kept away from open flame and spark sources. Piping system must regularly be checked for leaks. Always use safety glasses when connecting and disconnecting gas regulators and lines.

Sampling hazards

Product gases typically contain high levels of carbon monoxide and benzene, both of which are toxic and inhalation of fumes that may result from leaking gasifiers and sampling system pose an obvious health hazard to the workers. With adequate general laboratory ventilation short-term and long-term exposure levels will not be exceeded.

Acute toxicity hazards can also arise from leaks and solvent splashes from impingers caused by a rapid change in gas pressure.

A Plexiglas shield around the sampling system provides a suitable safety. Furthermore the use of a personal carbon monoxide detector is recommended.

7.3. Safety precautions

One key to prevent accidents is to use the safest possible practices in laboratory and on the plant. Only individuals with proper training and experience to deal with the expected risks and hazards during laboratory operations should therefore perform all chemical work.

All work spaces must be equipped with first aid kits, safety showers, eyewash fountains, fire extinguishers and fire blankets and a laboratory safety manual and Material Safety Data Sheets (MSDS) should be available. Plans for medical and chemical accident response must have been established and emergency telephone numbers must be readily available. Organic solvents shall be stored in specialised flammable and well-ventilated storage areas and chemicals should have well-ventilated storage places. The laboratory should be equipped with clean-

up equipment for chemical spills including appropriate absorbents (vermiculite[4], clay, dry sand, or towelling) for collecting and disposal containers.

Waste chemicals must be collected in suitable containers and stored in a properly ventilated place until disposed of according to safe disposal procedures that is commonly handled by a chemical hygiene officer.

The following basic personal safety rules should be followed when work on the plant orlaboratory is being conducted:

- Be instructed to the safety measurements and procedures of the plant by the operator. Discuss the configuration of the sampling equipment and the connection to the plant with the operator + check the compliance with the safety requirements of the sampling with the operator.
- Make sure that the ventilation system is switched on and is working before starting chemical work.
- Protective helmet should be worn at the sampling site.
- The sampling system should be checked for leaks before sampling.
- Wear eye protection (safety spectacles with side-shields, goggles, face-shield), protective gloves[5] and a chemical and fire-resistant laboratory coat as needed for the work at hand.
- Handle chemicals, solvent and samples in an efficient chemical fume cupboard.
- Carry out sampling in a well-ventilated area.
- Do not eat, drink or smoke in the laboratory or sampling area.
- Do not wear open shoes.

For more about this topic, the following Internet link may be useful: Chemical guide and permeation tables for laboratory gloves are available at http://www.pp.okstate.edu/ehs/hazmat/gloves.htm

7.4. Accidents

In the event of splashes on the skin, immediately rinse with water for 15 – 30 minutes and final cleaning with soap. In the event of large splashes on the body, remove contaminated clothing and promptly use the safety shower. Lipophilic substances can be rinsed of with polyethylene glycol. Splashes of chemicals in the eye are promptly flushed of with copious amounts of water for 15-30min using the eyewash and then seek medical advice.

Spills of chemicals should be cleaned up as they occur, using a suitable absorbent -dry sand or towelling- to collect and then dispose of residues according to safe disposal procedures.

Avoid breathing vapours of spilled chemicals and do not touch the spill without protective gloves.

7.5. Safety and health information resources

A broad coverage of chemical hazard topics is freely available on Internet resources. Here are some useful links:
- National Institute for Occupational Safety and Health (NIOSH) provides International Chemical Safety Cards (ICSCs) database including index with chemical names and synonyms. http://www.cdc.gov/niosh/ipcs/icstart.html
- The National Library of Medicine's Toxnet: http://toxnet.nlm.nih.gov/
- The United States Environmental Protection Agency (EPA) provides the Integrated Risk Information System (IRIS) database:
  http://www.epa.gov/iriswebp/iris/index.html
- Minimal Risk Levels (MRLs) for hazardous substances can be found at Agency for Toxic Substances and Disease Registry (ATSDR): http://www.atsdr.cdc.gov/mrls.html
- Chemical guide and permeation tables for laboratory gloves are available at http://www.pp.okstate.edu/ehs/hazmat/gloves.htm

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[4]: Hydrated magnesium-aluminium-iron silicate that can absorb large quantities of liquids.

[5]: There is no single glove material that is resistant to all chemicals and they should be chosen for each specific job. For compatibility and breakthrough characteristics of different glove material, an excellent information is *Guidelines for the Selection of Chemical Protective Clothing* published by the American Conference of Governmental Industrial Hygienists (ACGIH) or information provided by glove manufacturers.

Additional information about chemical characteristics and hazards can also be found in the following sources:
- Material Safety Data Sheets (MSDS) or International Chemical Safety Cards (ICSCs)
- Merck Index
- The Kirk-Othmer Encyclopaedia of Chemical Technology
- Sax's Dangerous Properties of Industrial Materials
- Bretheric´s Handbook of Reactive Chemical Hazards
- Patty's Industrial Hygiene and Toxicology
- Dictionary of Substances and their effects

8. References

- CEN Technical Specification "Biomass Gasification – Tar and Particles in Producer Gases – Sampling and Analysis", prepared by CEN task force BT/TF 143 WI CSC 03002.4TC, 2005
- Ramackers, Heynis, v.d.Weide; Engines and Adaptation of Engines for Producergas, The second international producer gas course and conference, Bandung, Indonesia, March 1985
- T.Milne, N.Abatzoglou and R.J.Evans; Biomass gasifier "tars": their nature, formation and conversion, Golden, CO (USA), NREL, NREL/TP-570-25357, 68 p., 1998

9. Appendices

9.1. Liquid Quench

The working principle of liquid quench with circulating fluid is shown in Figure 9-11. Liquid injection into the sample gas stream must occur immediately after the particle filter outlet. A liquid flow rate in the order 10 - 50ml/min (depending on the sample gas flow rate) is sufficient to cool the gas from 250 to 50°C.
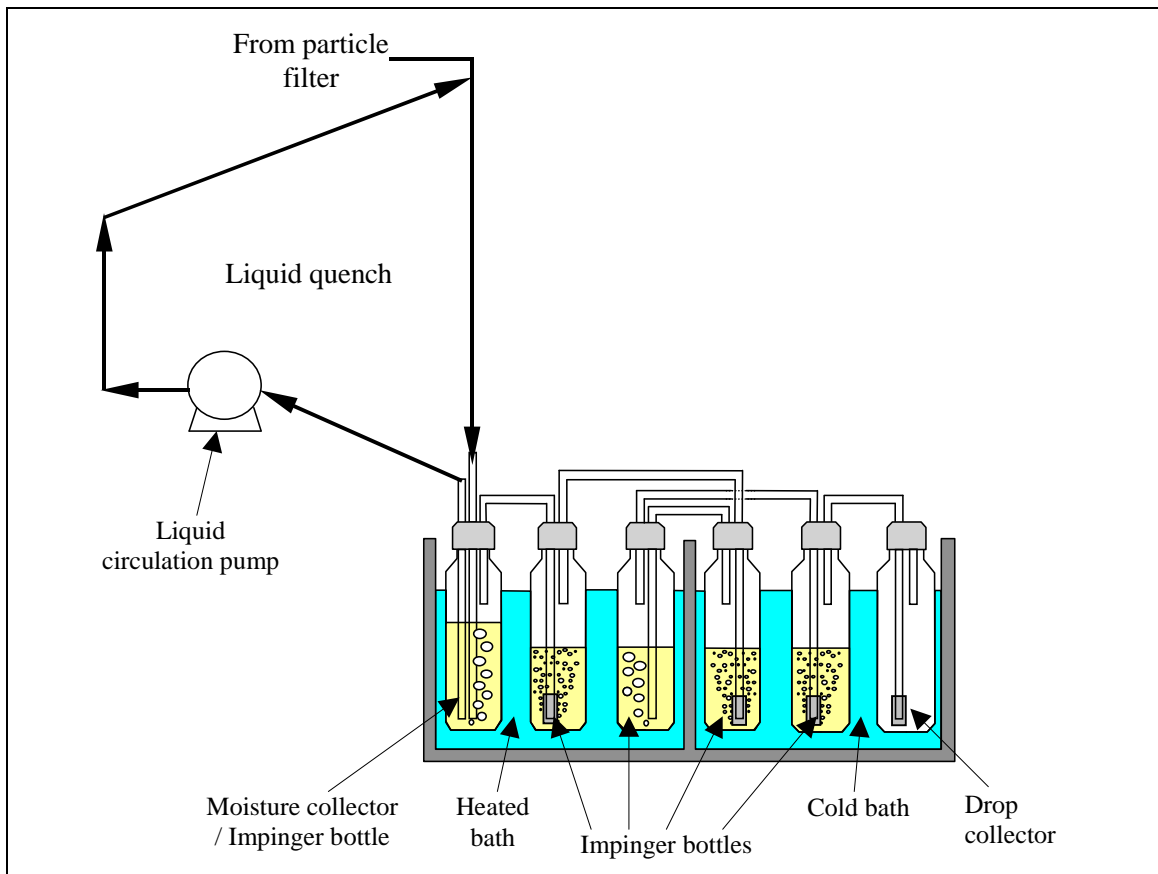
Figure 9-1: Example of a liquid quench system as part of the sampling train arrangement

9.2. Modified (VTT) design of Impinger Bottles

The mass and heat transfer in impinger bottles can be improved by modifying the design of impinger bottles. An modified design by VTT is shown in Figure 9-2. Glass bends using ball ground joints ensure correct connection of the impinger bottles. To ensure impinger bottle connections (conical and ball ground joints) are gas tight, only PTFE gaskets, PTFE tapes or solvent are accepted as the sealing media.
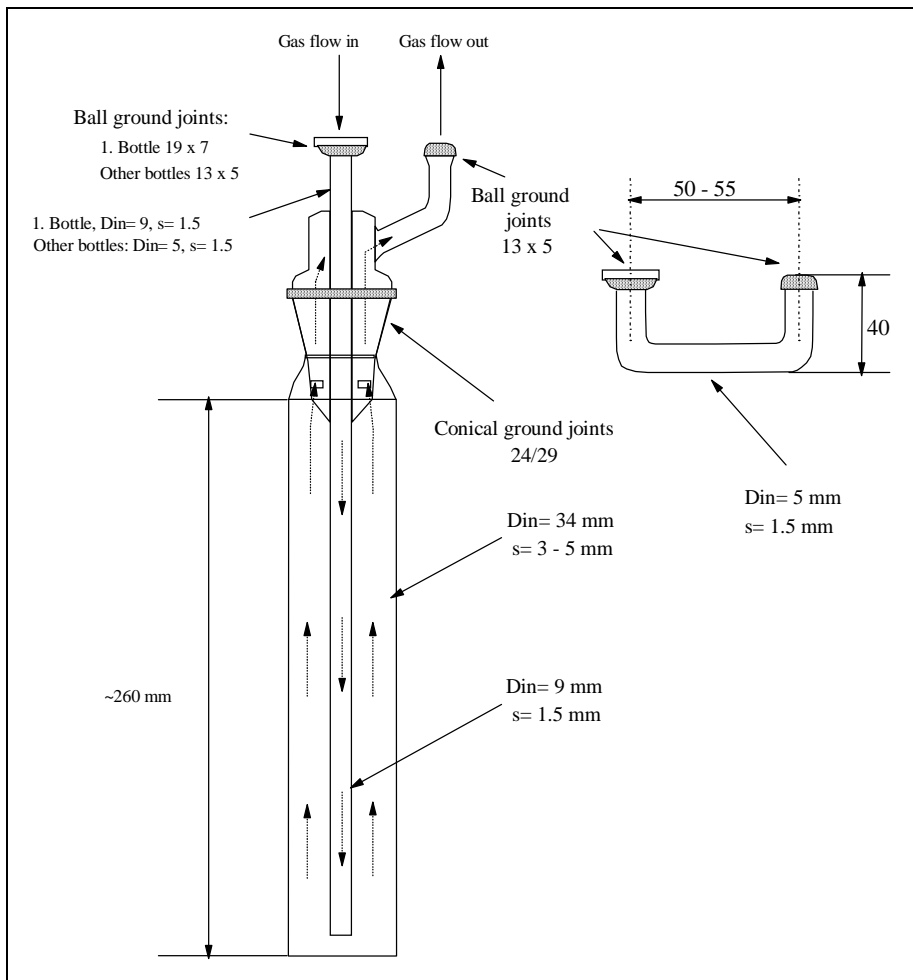
Figure 9-2:   The impinger bottle and the glass bend used by VTT.

9.3. General design and operating conditions of gasifiers

Gasification is a thermochemical process, which converts solid carbonaceous fuels into gas by mixing the fuel with an appropriate gasification agent. Most of the gasifiers fall into four categories (see Figure 9-3) based on the capacity and flow direction of the feedstock and the design, feedstock and on the gasification agent. These four types are:

1) Fixed-bed updraft (or countercurrent)

2) Fixed-bed down-draft (or cocurrent)

3) Fluidised-bed and

4) Entrained-flow.

Within the gasification reactor, the processes of fuel drying, pyrolysis, reduction and oxidation occur. The oxidative gasification agent converts char and tar from the pyrolysis process into gas. As the gas generation is an endothermic process, some of the gasification agent is required to supply the chemical energy by combusting a fraction of the fuel. The combustion process generally is internal.
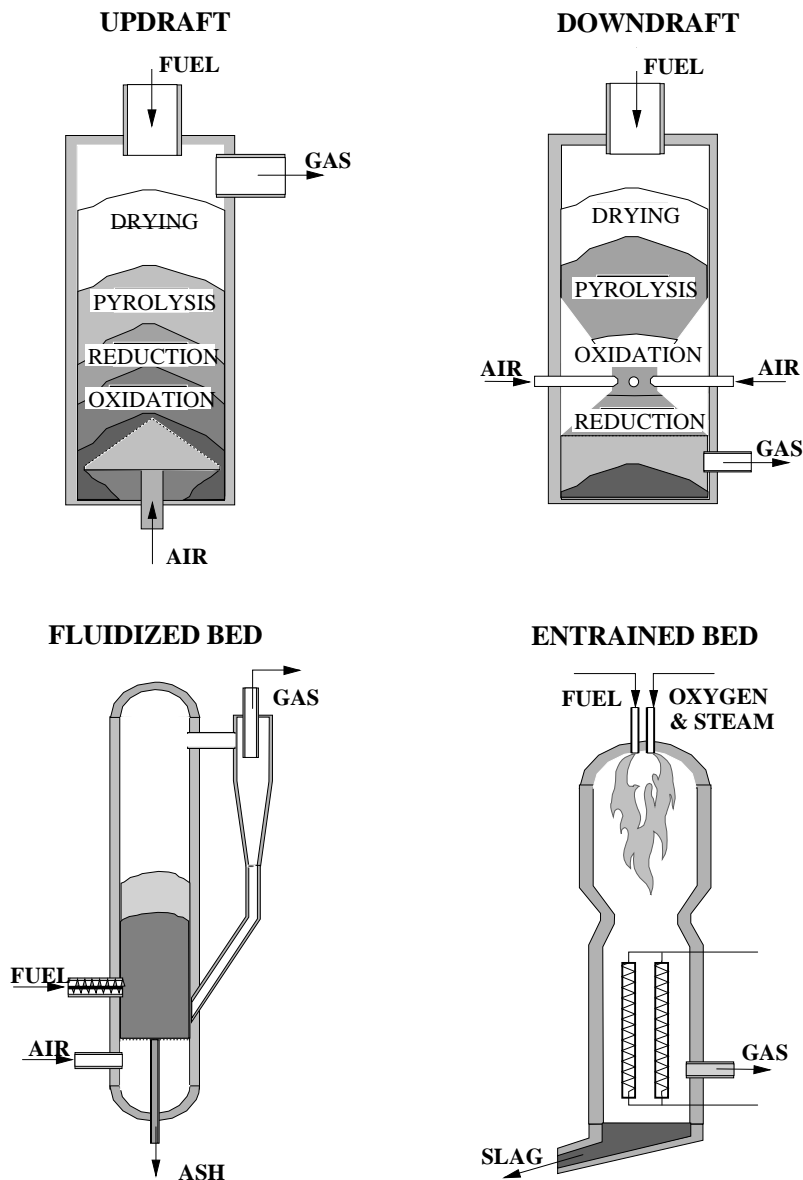
Figure 9-3: Schematic drawing of four basic gasifier types

In updraft gasifiers, the fuel generally moves from the top downwards and the gasification agent moves from the bottom upwards (updraft). As the gas leaves the reactor near the pyrolysis zone, the gas generated in updraft gasifiers exhibit a high level of organic components (tar). The solid carbon in the fuel is completely converted into gas and tar. Updraft gasifiers can be used for wet fuels and are relatively insensitive to the fuel size.

In cocurrent gasifiers, the fuel and gasification agent flow cocurrently, hence the gas leaves the reactor near the hottest zone and the tar levels are much lower than in updraft gasifiers. Also the amount of tar compoounds, present in updraft gasifier gas, is much higher than the amount of tar compounds present in downdraft or fluidised bed gasifier gas. A list of species that can be present is given in Appendix 9.4.

The cold gas efficiency (conversion of fuel carbon into non-condensable gases) of cocurrent gasifiers is generally higher than in updraft gasifiers. Generally, cocurrent gasifiers can only be used with dried fuel (typically 15 wt%) and the size of the fuel are in narrow limits.

With increasing expansion of the fuel bed, the reactor behaviour transforms from a fixed bed to a (stationary) fluidised bed (FB) reactor and further to a circulating fluidised bed (CFB) reactor. The highest heat and mass transfer rates are observed in CFB reactors. A further increase leads then to entrained flow reactor types. FB and CFB gasifiers are characterised by high gas throughputs and require dried fuel with sizes typically <2cm. CFB type gasifiers can be designed both for near atmospheric pressure and for pressurised applications.

Entrained flow gasifiers operate at elevated pressure and are found in coal gasification. The flow of fuel and gasification agent is cocurrent. In contrast with the other principles, the temperatures in the reactors are above the melting point of the ashes, which therefore leave the gasifier as molten slag.

In the Table 9-1, typical operating conditions and gas composition are displayed for some of the gasifier principles. No data were found for entrained flow gasifiers fuelled with biomass.

		Countercurrent	Cocurrent	CFB
Typical heat output	kW_{th}	1'000 − 10'000	100 − 1'000	>10'000
Fuel moisture	wt% (daf)	50	16	15
Typical gas composition				
Carbon dioxide (CO_2)	%	10.0	12.9	15.0
Carbon monoxide (CO)	%	20.0	18.0	15.4
Hydrogen (H_2)	%	14.0	14.2	14.8
Methane (CH_4)	%	2.5	1.9	4.2
Nitrogen (N_2, by diff.)	%	53.5	53.0	39.6
Typical contaminant levels				
Particles	g/m_n^3	0.1 − 0.5	0.1 − 1	20 - 60
Tar (generic definition)	g/m_n^3	50 − 150	0.5 − 2	7 − 10

Table 9-1: Typical operating conditions and gas compositions of various wood fuelled gasifiers at atmospheric pressure. Data source (tar and particles): Milne et al 1998

9.4. List of individual organic compounds

The next table gives the names, CAS-registry numbers and boiling points of individual organic compounds that are determined in biomass gasification product gases. The list of compounds as given by this table is not exhaustive. The list is explicitly not a list of compounds to be determined by this Technical Specification, hence this is an informative list. See also Chapter 1 "Scope" and Annex A and Annex B of the Technical Specification, in which the compounds are mentioned for which the Technical Specification applies.

Table 9-2- List of individual organic compounds to be found in biomass gasification product gases

Group / common name	Other / (more) trivial name	Chemical Abstract Service (CAS) Registry Number	Boiling point (°C) (Handbook of Chemistry and Physics, vol. 77)
Acids			
Formic acid	Methanoic acid	64-18-6	101
Acetic acid	Ethanoic acid	64-19-7	117,9
Propionic acid	Propanoic acid	79-09-4	141,1
Butyric acid	Butanoic acid	107-92-6	163,7
Sugars			
Levoglucosan	1,6-amhydro-beta-D-Glucopyranose		
Alpha-D-Glucose	Alpha-D-Glucopyranose	604-68-2	Sub[1]
Beta-D-Fructose	Beta-Levulose	53188-23-1	
Cellobiosan			
Alcohols			
Methanol	Methyl alcohol	67-56-1	64,6
Ethanol	Ethyl alcohol	64-17-5	78,2
Aldehydes and ketones			
Formaldehyde	Methanal	50-00-0	-19,1
Acetaldehyde	Ethanal	75-07-0	20,1
Acetone	2-Propanone	67-64-1	56,0
2-Cyclopenten-1-one	Cyclopenten-3-one	930-30-3	136
(Methyl)- 2-Cyclopenten-1-one	(2- 3- 5-) methyl-2-cyclopenten-1-one	1120-73-6, 2758-18-1, 14963-40-7	157; 157,5; 140
Phenols			
Phenol	Hydroxybenzene	108-95-2	181,8
Cresols (o, m or p)	(2-, 3- or 4-)methyl-phenol	95-48-7, 108-39-4, 106-44-5	191,0; 202,2; 201,9
Xylenols	(2,3- 2,4- 2,5- 2,6- 3,4- or 3,5-) dimethylphenol	526-75-0, 105-67-9, 95-87-4, 576-26-1, 95-65-8, 108-68-9	216,9; 210,9; 211,1; 201,0; 227;, 221,7
Butylphenols	(2-, 3- or 4-)butyl-phenol	3180-09-4, 4074-43-5, 1638-22-8	235; 248; 248
Methylbutylphenols	2-butyl-4-methyl-phenol	6891-45-8	228
Naphthols	(1- 2-) Naphthol or -Naphthalenol	90-15-3, 135-19-3	288; 285
Methylnaphthols	4-methyl-1-naphthol, 1-methyl-2-naphthol	10240-08-1, 1076-26-2	166; 160
Guaiacols			
Guaiacol	2-methoxy-phenol	90-05-1	205
Creosol = 4-methyl-guaiacol	2-methoxy-4-methyl-phenol	93-51-6	221
Ethylguaiacol	2-methoxy-4-ethyl-phenol	2785-89-9	236,5
Eugenol	2-methoxy-4-(2-propenyl)-phenol	97-53-0	253,2
Isoeugenol	2-methoxy-4-(1-propenyl)-phenol	97-54-1	266

Furans

Dimethylfuran	(2,4- 2,5-)dimethylfuran	3710-43-8, 625-86-5	94; 93,5
Furfural (2-furaldehyde)	2-Furancarboxaldehyde	98-01-1	161,7
Methyl Furfural	5-Methyl-2-furancarboxaldehyde	620-02-0	187
Furfuryl alcohol	2-Furanmethanol	98-00-0	171
Benzofuran	Coumarone	271-89-6	174
Methylbenzofurans	(2- 3- 5- 7-) methylbenzofuran	4265-25-2, 21535-97-7, 18441-43-5, 17059-52-8	197,5; 197; 198; 190,5
Dimethylbenzofurans	(2,5- 2,6- 2,7- 3,5- 3,6- 4,6- 4,7- 5,6- 5,7- 6,7-) dimethylbenzofuran	29040-46-8, 24410-51-3, 59020-74-5, 10410-35-2, 24410-50-2, 116668-34-9, 28715-26-6, 24410-52-4, 64965-91-9, 35355-36-3	220; 217,5; 216; 220,5; 222; 219; 216; 221; 222; 218
Dibenzofuran	2,2'-biphenylene oxide	132-64-9	287
Methyldibenzofurans			

Mixed oxygenates

Glyoxal	Ethandial	107-22-2	50,4
Hydroxyacetaldehyde	(Hydroxyethanal, glycolaldehyde)	141-46-6	
Propanal-2-one	(methyl glyoxal, 2-oxopropanal, pyruvaldehyde)	78-98-8	72
Acetol	1-hydroxy-2-propanone	116-09-6	145,5
2-hydroxy-3-methyl-2-cyclopentene-1-one			
Methoxybenzene	Anisol	100-66-3	153,7
Dimethoxybenzenes	(1,2- 1,3- 1,4-) dimethoxybenzene	91-16-7, 151-10-0, 150-78-7	206; 217,5; 212,6
Trimethoxybenzenes	(1,2,3- 1,3,5-) trimethoxybenzene	634-36-6, 621-23-8	235; 255,5
Trimethoxyphenols			
Vanillin	4-hydroxy-3-methoxybenzaldehyde	121-33-5	285

Aromatic compounds

Benzene		71-43-2	80,0
Toluene	Methylbenzene	108-88-3	110,6
Xylenes (o, m and p)	(1,2- 1,3- and 1,4-)dimethylbenzene	95-47-6, 108-38-3, 106-42-3	144,5; 139,1; 138,3
Ethynylbenzene		536-74-3	143
Styrene	Ethenylbenzene	100-42-5	145
4-Methylstyrene	1-ethenyl-4-methyl-benzene	622-97-9	172,8
Indene (1H-Indene)	Indonaphthene	95-13-6	182
Methylindene	(1- 2- 3- 4- 6- 7-)methyl-1H-indene	767-59-9, 2177-47-1, 767-60-2, 7344-34-5, 20232-11-5, 7372-92-1	199; 206; 198; 209; 207; 209

PAHs (* indicate EPA list of 16 PAHs)

Naphthalene[*]		91-20-3	217,9
(1- or 2-) Methylnaphthalene		90-12-0, 91-57-6	244,7; 241,1
Diphenyl	1,1-Biphenyl	92-52-4	256,1
Acenaphthylene[*]	Acenaphthalene	208-96-8	280; 150[2]
Acenaphtene[*]	1,2-dihydro-Acenaphthylene	83-32-9	279
Fluorene[*] (9H-Fluorene)	2,2'-Methylenebiphenyl	86-73-7	295
Phenanthrene[*]		85-01-8	340
Anthracene[*]		120-12-7	339,9
Fluoranthene[*]	1,2-(1,8-Naphthylene)benzene	206-44-0	384
Pyrene[*]	Benzo(def)phenanthrene	129-00-0	404
Benzo(a,b,c) fluorene	11H-Benzo(a)fluorene	238-84-6	405
Benzo(a)anthracene[*]	1,2-Benzanthracene	56-55-3	-
Chrysene[*]	1,2-Benzophenanthrene	218-01-9	448
Benzo(b[*], j or k[*]) fluoranthene	B.(b)fl.=Benz(e)acephenanthrylene B.(j)fl.=Dibenzo(a,jk)fluorene B.(k)fl.=2,3,1',8'-Binaphthalene	205-99-2, 205-82-3, 207-08-9	-; -; 480
Benzo(a[*] or e)pyrene	(2,3- 1,2-)Benzopyrene	50-32-8, 85-02-9	-; 352

Dibenzo(a,h)anthracene*	1,2,5,6-dibenzanthracene	53-70-3	-
Perylene	Dibenzo(de,kl)anthracene	198-55-0	-
Indeno(1,2,3-cd)pyrene*			
Benzo(g,h,i)perylene*	1,12-Benzperylene	191-24-2	-
Dibenzopyrenes			
Anthanthrene			
Coronene		191-07-1	525
Nitrogen containing aromatics			
Pyridine	Azine	110-86-1	115,2
Methylpyridines, Picolines	(2- 3- 4-)Methylpyridine (2- 3- 4-)Picoline	109-06-08, 108-99-6, 108-89-4	129,3; 144,1; 145,3
Quinoline	1-Azanaphthalene	91-22-5	237,1
Isoquinoline	Benzopyridine	119-65-3	243,2

[1]: sublimates

9.5. Example test and analysis logs for sampling and result documentation

9.5.1. Parameter log for sampling of P&T

Sampling of P&T from Biomass Producer Gases						
					Examiner:	X
Gasifier Type/Site:		X			Date:	X
Test No.:		X				
Gasifier parameter						
Actual power output:			kW	(max. .... kW)		
(based on fuel fuel input)						
Raw gas flow rate (dry):			[m_n^3/h] (if calc., spec. gas rate:			m_n^3/kg **wet**
Gasifier start *:				stationary since *:		
Fuel type *:						
Fuel moisture *:			[%, dry basis]			
Actual fuel feeding rate *:			[kg wet/h]			
Sampling parameters						
Sampling site (hot/cold end):						
Tar trapping solvent:						
Ambient temperature:			[°C]			
Ambient pressure:			[mbar]			
Duct diameter:			cm			
Diameter of sampling nozzle:			mm			
Particle filter temperature:			[°C]	Filter tube no.:		
		init. weight	final weight			
Solvent stock bottle:						
Solvent storing bottle:				[g]		
Summary protocol						
Solvent from P&T sampling:			[g]			
Approx. mass of condensate:			[g]			
Solvent from Soxhlet extraction:			[g]			
Total particle mass in filter tubes:			[mg]			
Normalised sampled gas flow rate:			[m_n^3/h]			
Remarks:						

9.5.2. Parameter log for gas meter reading

Sampling of P&T from Biomass Producer Gases

Gasifier Type/Site:		X			
Sampling site (hot/cold end):				Date:	X
Test No.:		X			
Rated sampling gas flow rate (dry):			m_n^3/h (calculated set point;		
10% over isokinetic)					
P+T sampling start:			P+T sampling end:		

			Temperature in gas meter	Pressure In gas meter		
Gas meter protocol			[°C]	bar		
Time	Gas temperature	Reading			Δp pump	Sampling
	in duct	gas meter				Flow rate
[hh:mm]	[°C]	[m^3]			[mbar]	[m_n^3/h]

Remarks:						
Averaged sample flow rate:			m_n^3/h			
Total amount of gas sampled:			m_n^3			
Total sampling duration:			hours			
Mean gas meter temperature:			°C			

9.5.3. Log for particulate measurement

Sampling of P&T from Biomass Producer Gases						
Gasifier Type/Site:		X			Date:	X
Sampling site (hot/cold end):					Test No.:	X
Particle filter pre-treatment						
Type of particle filter used:					Filter tube no.:	
Preconditioning temperature:			°C			
Preconditioning duration:			hours			
Initial tube weight after preconditioning:			g			
Tar extraction from particle filter with Isopropanol						
Soxhlet extraction		Start:			hh:mm	
		End:			hh:mm	
		Duration:			hours	
	tara weight	**gross weight**		**net weight**		
Storing bottle					[g]	
Remarks:						
Particle filter post-treatment						
Post-conditioning temperature:			°C			
Post-conditioning duration:			hours			
Final tube weight after post-conditioning:			g			
Remarks:						

9.5.4. General logbook of test performer

This chapter contains the information mentioned in the logbook of the test performer. It describes all the relevant aspects regarding the sampling site, the sampling and analysis procedures should be given.

The following information should be given in a number of log-parts:

- Installation description (type of gasifier, gas cleaning, capacity, year of construction .....)
- Fuel characterisation (origin, moisture, size (distribution) .....)
- Description of sampling site and (gasifier) operation conditions
- Sampling train set-up (arrangement of type of modules used)
- Sampling (duration, temperatures, pressure, flow rate ....)
- Sample(s) post treatment
- Type of analysis used (incl. calibration methods)
- Tables with results