Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases

Version 3.3

J.P.A. Neeft, H.A.M. Knoef, U. Zielke, K. Sjöström,
P. Hasler, P.A. Simell, M.A. Dorrington, L. Thomas,
N. Abatzoglou, S. Deutch, C.Greil,
G.J. Buffinga, C. Brage, M. Suomalainen

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European Commission (DGXII)
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1. Abstract

This Guideline provides a set of procedures for the measurement of organic contaminants and particles in producer gases from biomass gasifiers. The procedures are designed to cover different gasifier types (updraft or downdraft fixed bed or fluidised bed gasifiers), operating conditions (0 - 900°C and 0.6 - 60 bars) and concentration ranges (1 mg/m_n^3 to 300 g/m_n^3).

The Guideline describes a modular sampling train, and a set of procedures, which include: planning and preparation of the sampling, sampling and post-sampling, analysis, calculations, error analysis and reporting.

The **modular sampling train** consists of 4 modules. Module 1 is a preconditioning module for isokinetic sampling and gas cooling. Module 2 is a particle collection module including a heated filter. Module 3 is a tar collection module with a gas quench (optionally by circulating a liquid), impinger bottles and a backup adsorber. Module 4 is a volume-sampling module consisting of a pump, a rotameter, a gas flow meter and pressure and temperature indicators. The equipment and materials that are required for procuring this modular sampling train are given in the Guideline.

The **sampling** procedures consist of a description for isokinetic sampling, a leakage test prior to sampling, the actual sampling and its duration, how the equipment is cleaned after the sampling, and how the samples are prepared and stored.

Analysis of the samples is performed via three procedures. Prior to these procedures, the sample is prepared by Soxhlet extraction of the tars on the particle filter and by collection of all tars in one bulk solution. The first procedure describes the weighing of the particle filter to obtain the concentration of particles in the biomass producer gas. The bulk tar solution is used for two purposes: for determination of gravimetric tar and for analysis of individual compounds. The second procedure describes how to determine the gravimetric tar mass from the bulk solution. The third procedure describes how the solution can be analysed by GC-MS or GC-FID to obtain the concentrations of individual tar compounds.

2. Aim of this Guideline

This Guideline is aimed to give a set of procedures for the measurement of organic contaminants and particles in producer gases from biomass gasifiers. Biomass gasifiers can be updraft fixed bed gasifiers, downdraft fixed bed gasifiers and fluidised bed gasifiers, operating under atmospheric or pressurised conditions. The Guideline is aimed to measure organic contaminants and particles in the concentration range typically from 1 mg/m_n^3 to 300 g/m_n^3 at all relevant conditions (0 - 900°C and 0.6 - 60 bar).

As organic contaminants ("tars") from pyrolysis or gasification of coal are similar in nature compared to (high temperature) biomass gasification tars, also coal tars can be measured with this Guideline.

The procedures and methods described in this report differ from most of the methods used for sampling organic compounds present in the gaseous emissions from various industrial processes such as flue gases or automobile exhaust gases. The differences are related to the fact that the concentration level of the organic species present in the producer gases exceed the concentrations found in flue gases generally by more than 3 orders of magnitude. Hence the methods described within this Guideline are not intended to be applicable for sampling organic components in trace concentrations (ppm or sub-ppm range).

The Guideline, previously entitled 'Protocol', has now been changed to 'Guideline' thus providing a 'temporary status'. A standardisation trajectory at CEN has been initiated, with the aim to convert the Guideline to a Standard.

The Guideline describes sampling and analysis of organic contaminants in product gases from gasification of biomass. Biomass in this Guideline is defined as uncontaminated organic materials of non-fossil origin. The Guideline can also be applied for non-biomass materials (that is: for sampling and analysis of organic contaminants from gasification of *contaminated* organic materials of non-fossil origin, such as waste wood, sludge and manure). However, this can only be undertaken for analysis of the same compounds that are found from uncontaminated organic materials. In other words: The Guideline is not specifically designed to measure organics formed from gasification of the contaminated organic materials or from interactions between these contaminants and gasification products of the biomass. Examples of such organic contaminants are halogenated compounds, monomers of degradation of plastic materials, and compounds containing nitrogen and sulphur apart from the most common ones also found in biomass producer gases listed in Appendix 13.2.

3. Definitions

b.p.:	Boiling point
Biomass:	Uncontaminated organic materials of non-fossil origin such as wood, straw or short rotation forestry fuels
BTX:	Benzene, Toluene and Xylenes
GC-FID	Gas Chromatography – Flame Ionisation Detector
GC-MS	Gas Chromatography – Mass Spectrometer
Gravimetric tar:	Evaporation/distillation residue from particle free sampling solution(s) determined by gravimetric analysis (see Chapter 8.1.4)
IC engine:	Internal Combustion Engine
Organic compounds:	Generic term for individual organic compounds listed in Appendix 13.3
Producer gas:	Gas produced from thermal biomass conversion reactor (gasifier). May include also pyrolysis gas
Particles:	Solid residue from particle filter after solvent extraction or solid residue from filtration of sampling solution(s) (Chapter 8.1.4)
Main gas stream:	Producer gas stream in gas pipes of gasification reactor
Normal conditions:	273.15 K, 101325 Pa = 1.01325 bar, dry (according to DIN 1343)
Slip gas stream:	Representative (small) part of the main gas stream
Tar:	Generic (unspecific) term for entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 through C6). Benzene is not included in tar.
VOC:	Volatile organic compounds. Generic term for organic compounds (e.g. with b.p. < 250°C) which exhibit a considerable vapour pressure at room temperature. VOC represent the lower boiling fraction of gaseous hydrocarbons (C1 through C6) and tar.
XAD:	Not an abbreviation of a substance. XAD is a registered trademark of Rohm & Hass (It). XAD is a resin of polystyrene (XAD-2 and XAD-4) or polyacrylic (XAD-7 and XAD-8).
PTFE:	Polytetrafluoroethene

4. Units and indices

Notation and units (in agreement with ISO 9096):

Sign	**Parameter**	**Unit**
a	Linear coefficient	-
a	Effective nozzle area	m^2
A	Surface area	m^2
C	Mass fraction of carbon	-
c	Concentration in producer gas	kg/m_n^3
cc	Carbon content (non-condensable gases = CO, CO_2, CH_4, C_2H_2, C_2H_4 etc.)	kg C / m_n^3 or kg C / kg biomass[1]
d	(Inner) diameter	m
Δ	Error	
f	Water vapour concentration	kg/m^3
H	Mass fraction of hydrogen	-
$\dot{m}$	Mass flow (of fuel, ash, producer gas)	kg / h
M	Mass	kg
N	Number	-
p	Absolute pressure	Pa or bar
P_0	Pressure at normal conditions: 101325 Pa = 1.01325 bar (according to DIN 1343)	Pa or bar
p_{am}	Ambient pressure	Pa or bar
Δp	Differential pressure	Pa or bar
q_m	Mass flow rate	kg/h on dry basis
q_V	Volumetric flow rate	m_n^3/h
RF	Response Factor	
ρ	Density	kg/m^3
σ	Standard deviation	
t	Sampling time (total)	h
cc	Carbon content (non-condensable gases = CO, CO_2, CH_4, C_2H_2, C_2H_4 etc.)	kg C / m_n^3 or kg C / kg biomass[1]
T	Temperature (absolute)	K
T_0	Temperature at normalconditions: 273.15 (according to DIN 1343)	K
Θ	Temperature	°C
ν	Velocity	m/s
V	Volume	m_n^3
$\dot{V}$	Gas volume flow rate	m_n^3/ hr
v	Velocity of producer gas in duct	m/s
Y_{gas}	Gas yield	m_n^3/kg biomass[1]
<>	Average	

[1]: Biomass on dry and as-free (daf) basis

Used subscripts:

Sign	Subscript means
A	Individual compound
a	Actual conditions in sampling plane
act	Actual, measured at the gas meter
agent	Gasification agent
ash	Solid residue from gasification process
drygas	Dry producer gas (not including H_2O)
c	Compound
D	Main gas duct
F	Particle filter
fuel	Solid biomass
g	Any gas measuring devise
gas	Producer gas
gasif. agent	Gasification agent/agents
H_2Ogas	Water in the producer gas
i	Individual value
is	Internal standard
N	Sample nozzle
n	Normal conditions (DIN 1343, in English often called standard conditions)
p	Quantity of particles
<p>	Average pressure
particles	Particles in producer gas
p,0	Dry clean particle filter
p,l	Dry loaded particle filter obtained after sampling and Soxhlet extraction
Pt	Pitot tube
s	Compound
sol	Quantity in the tar solution sample
solid	Solid residues from gasification (bottom ashes, fly ash)
tar	Organic compounds in producer gas
T	Quantity of “Gravimetric tar”
w	Water vapour
0	Start of the sampling procedure
1	Stop of the sampling procedure

Sign	Superscript means
‘	Moisture included

5. Measuring principle

5.1. 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 of isokinetic sampling of flue gases are given in the standards ISO 9096 or VDI 2066.

The aim of the principle has been to keep it as simple as possible. This is because the measuring conditions can vary from ‘comfortable’ laboratory rooms to an executive plant gasifier where there is no customised room for measurements or measurement apparatus. Also the weather conditions can be challenging, for instance in northern Europe measurements might 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 containing a solvent for tar absorption. The bottles collecting tar are placed in a cold bath so that gradual cooling of the sampled gas from about 20°C to the final temperature - 20°C 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 train set-up with solvent impingers is designed for flow rates up to 0.6 m_n^3/h.

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. In updraft gasification the temperature of the sampling line and the particle filter should be 100-125°C, whereas in downdraft and fluidised-bed gasification 300 – 350°C has been found as suitable temperatures

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

Immediately after sampling the content of the impinger bottlesis decanted into a storage bottle. 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 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 MWth) 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 than 0.6 m_n^3/h when using the minimal nozzle diameter of 4 mm. 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 necessary when only tar is sampled and when the gas temperature under study at the sampling site exceeds 350°C. Such temperatures generally safely avoid tar condensation in the form of aerosols and/or droplets and also minimises adsorption of organic species on particles.

For non-isokinetic sampling the alignment of the probe in relation to the gas flow is not so stringent, also more freedom is available for the design of the probe nozzle to reduce blockages. This is important especially in pressurised gasification since the probe cannot be removed from the gas line during operation.

5.2. Basic concept of the sampling train

The modular sampling train consists of 4 main modules and respective submodules. The main modules are gas preconditioning, particle collection, tar collection and volume measurement.

In the preconditioning module (Module 1) the process gas is cooled or heated, depending on the process temperature, to a constant temperature of 300-350°C using a heated probe. For updraft gasifiers a temperature of 100-125°C should be chosen. With pressurised gasification the pressure is reduced to atmospheric pressure. The module includes an airtight (sealed) lock.

In the particle collection module (Module 2) a heated filter, maintained at the same temperature as the probe, collects the solids from the gas.

The tar collection module (Module 3) consists of three submodules. In the first submodule the gas is cooled and moisture and some of the tar is collected in a condenser at a temperature of approximately 20°C. The use of a liquid quench, which facilitates cleaning of sampling lines after the sampling, is optional. In the second submodule tar and VOCs are absorbed into the solvent at -20°C in a series of impinger bottles. In the third and optional submodule a backup VOC adsorber collects residual VOC's which may have penetrated the impinger train. The backup VOC adsorber is not necessary when enough impinger bottles, appropriate solvents and collection temperatures are used.

The volume-sampling module (Module 4) consists of three submodules. The purpose of these submodules is to: (a) maintain the sample flow by a pump (not needed in pressurised gasification); (b) adjust and control of flow rate; (c) measure the sample volume; and (d) vent the gas.

The concept of the modular sampling train is shown in Figure 5-1. Table 5-1 summarises the function of each module.

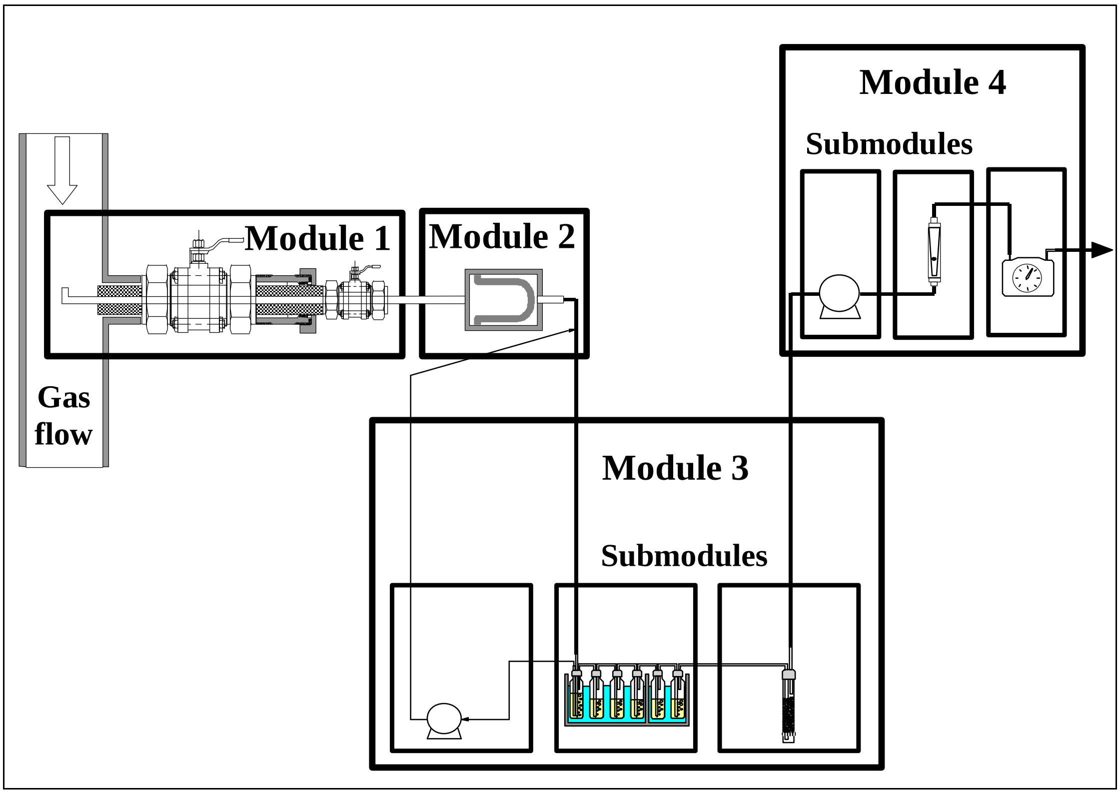

Figure 5-1: Concept of the modular sampling train. The liquid quench is optional.

	Function	**Equipment**
Module 1 (Gas preconditioning)	Gas cooling, pressure letdown	Nozzle, valves, sampling lines
Module 2 (Particle collection)	Separation and collection of solids	Heated filter (high temperature)
Module 3 (Tar collection)		
SubModule 3.1	Moisture and partial tar condensation	Condenser at 20°C
SubModule 3.2	Tar and VOC collection	Impingers with solvent at T < -20°C
SubModule 3.3	Backup VOC sampler	Adsorber tower (act. carbon, XAD, others) at T_{amb} or lower
Module 4 (Volume sampling)		
SubModule 4.1	Gas suction	Pump
SubModule 4.2	Gas volume integration	Gas meter, needle valve (adjustment and control of flow rate), pressure and temperature indicators
SubModule 4.3	Vent/exhaust gas handling	Outdoor ventilation

Table 5-1: General description of modules and submodules with purpose and equipment used

5.3. Description of sampling module 1 (gas preconditioning)

5.3.1. General

The sampling line consist of a sampling probe (the part that enters gasification conditions), 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, cleaning of the line, sufficient cleaning of sample gas and prevention of condensation should be considered.

5.3.2. 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. Both straight-ended nozzles and those angled at 45° can be used.

Isokinetic sampling requires a special probe. The design of such a probe is described in Paragraph 6.3.

5.3.3. Gas preconditioning for atmospheric gasifiers

The sampling line for an atmospheric process is shown in Figure 5-2.

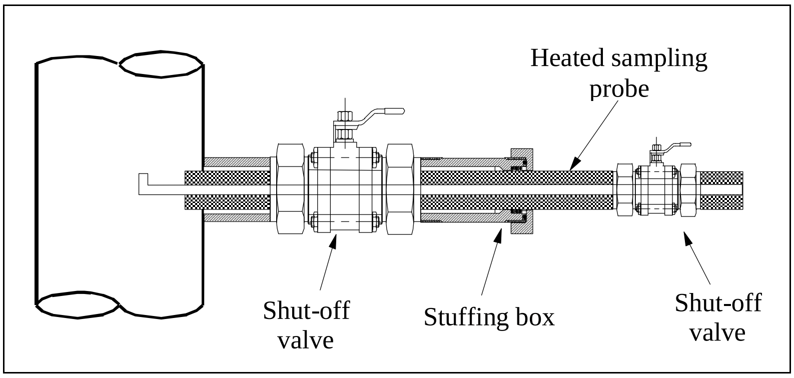

Figure 5-2: Sampling line for gases containing solid and gaseous impurities at atmospheric pressure.

The sampling line 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 shown in more detail in Paragraph 6.4. 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). Electrical heating of the sampling line 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 tar only is measured, the particle removal from the sample gas can be carried out also 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.

5.3.4. 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 5-3). The whole sampling line is heated and tar is sampled at ambient pressure.

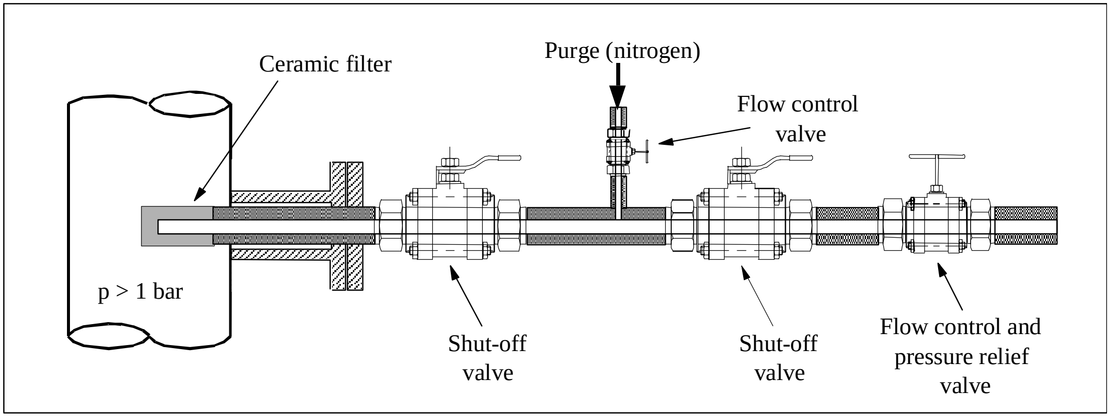

Figure 5-3: An example of a sampling line for a pressurised process for tar measurement only

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 (maximum 400°C) 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 a steadier pressure relief and higher reliability in service (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 flow of sample gas is regulated by the last control valve in the line, from which the gas is led through a PTFE hose or through a glass pipe into the condenser. This line should be kept to a minimum length.

Condensation of water vapour and condensable gases before the condenser is prevented by electrically heating the sampling line to 300-350°C. This will prevent 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. Quartz and fibreglass filters can be used as hot filters. 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.

5.4. Description of sampling module 2 (particle filter)

Particles are collected in an external heated filter system. Quartz filters (absolute filters) must 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[1]).

Plate filters are used for particle concentrations below 20 mg/m_n^3 (VDI 2066, part 7). The recommended minimum diameter for the plate filter is 90 mm.

For particle concentrations above 20 mg/m_n^3, filter thimbles are used. Dimensions of filter thimbles are selected for subsequent Soxhlet extraction procedures. The recommended dimensions for the filter thimble are a 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. This is valid for sample flows of 0.6 m^3_n/h and for producer gases containing high temperature tar.

The filter holder must be gas tight. An example of a possible way to mount the filter is shown in Figure 5-4.

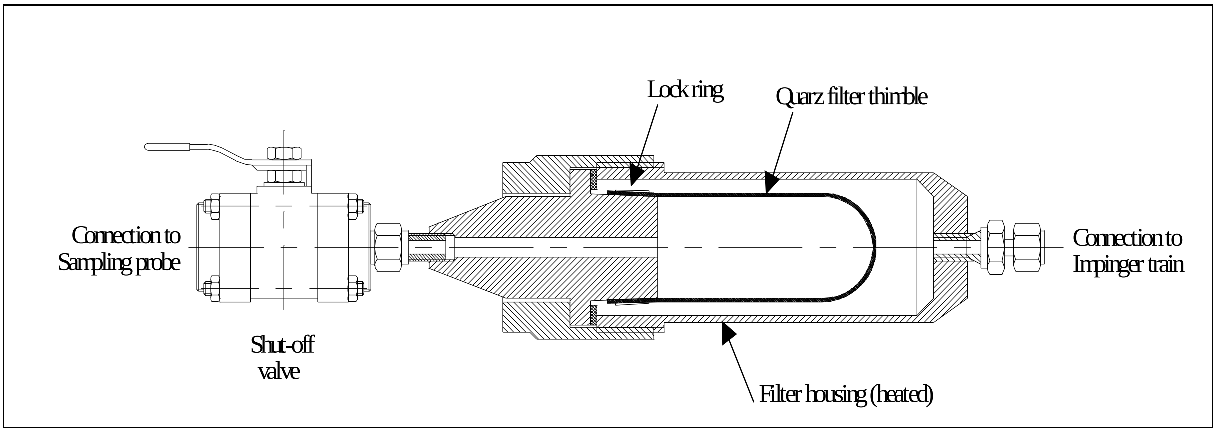

Figure 5-4: Module 2: the heated particle filter. This figure shows one of the possible ways to mount the thimble filter in the housing.

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 is (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 and has to 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. Operating temperatures are given in Paragraph 5.8.

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, since SiC has very little or no catalytic effects on tar decomposition. Reverse flow, high-pressure nitrogen purge should be available to clean the SiC filter from particles.

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[1]: 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.

The temperature of the stainless steel filter holder (AISI 310, AISI 316) and the SiC filters should be < 700°C to prevent any catalytic change in the concentrations of tar compounds.

5.5. Description of sampling module 3 (tar collection)

The module 3 is schematically shown in Figure 5-5.

The connection between the hot metal tubing and the impinger bottle should be designed accurately to assure the tightness of the joint. The joint can be practised for instance in the following way. The end of the metal tubing is formed 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 similar glass joint. The smaller radius makes the cracking of the glass female joint due to different thermal expansion less likely, but then special attention is needed to the sealing of the joint.

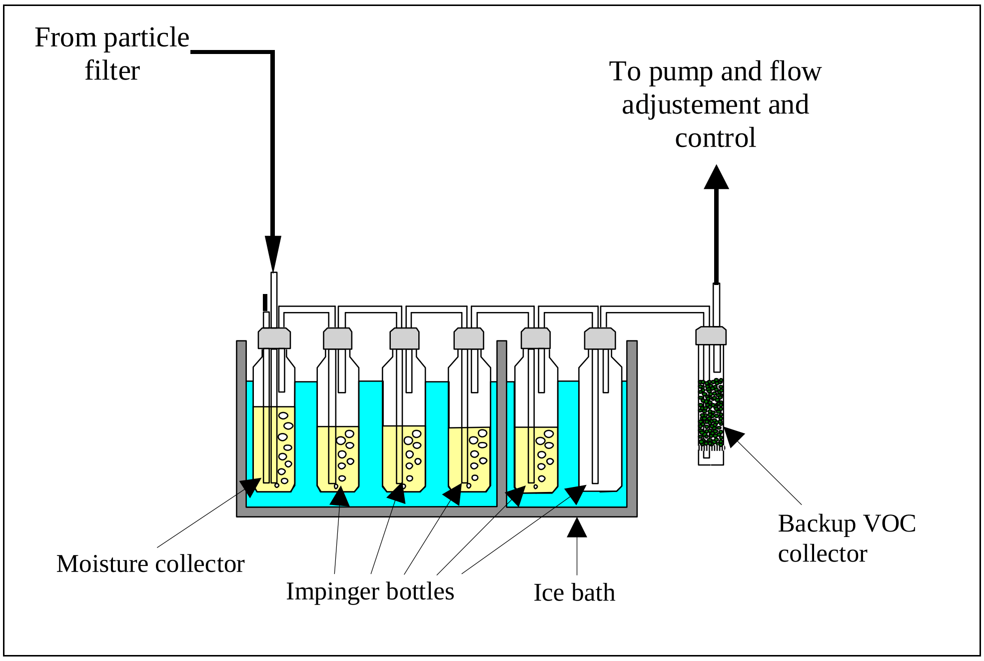

Figure 5-5: Module 3 of the sampling train: impinger bottles and VOC collector

5.5.1. Moisture collector

In the moisture collector, water and tar are condensed from the process gas by absorption in isopropanol at 20°C. 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 designed to meet the demands of the gasifier (see also Chapter 7).

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. The end of the metal tubing connected to the impinger bottle is formed identical to the male glass joint so that it fits the female ground joint of the impinger bottle. When using a liquid quench, isopropanol is the circulating liquid. The working principle of the liquid quench is described in Appendix 13.4.

5.5.2. Liquid tar impingers

After the moisture collector the gas is passed through a series of impingers (at least 3, preferentially 5) each containing approximately 50 ml of solvent. Direct condensation of the liquid effluent without diluting media, e.g., with cold trapping, can result in further reactions of the trapped compounds.

Optionally measures can be taken to disperse the gas flow and thus enhance both mass and heat transfer. One possible measure is the use of glass beads, which can be used in all impingers or in some only. The impinger bottle is half-filled with glass beads. Another possibility is the use of glass frits, either as large as the diameter of the impinger bottle or mounted as filter to the bottom of the impinger bottle gas inlet tube. Fine-meshed frits give better results than coarse-meshed frits, it is recommended to install at least one G3 frit in the impinger train.

Standard glass impingers (100 ml or 250 ml volume) with an inner tube diameter of 4 mm are used. Alternatively, it is also possible to use a modified impinger design as shown in Appendix 13.5.

Temperatures of the impinger bottles are 20°C for the moisture collector and the first three impinger bottles, and -15 or -20°C for the last two impinger bottles. 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.

5.5.3. Backup VOC sampler

The optional backup VOC sampler collects the residual solvent or VOC’s which may have penetrated the impinger train. The backup VOC adsorber is unnecessary when using several impingers in series, appropriate solvents and collection temperatures. It is primarily used as a pump and volume metering protection device. The backup VOC sampler contains an adsorbent such as activated carbon, XAD or Tenax. The temperature of the adsorbent should be kept low (< 50 °C) to prevent decrease in sampling capacity. With XAD or Tenax, the compounds, which have penetrated the tar impingers, can be recovered and analysed.

5.5.4. Alternative sampling train

During preparation of the Guideline, the partners have gathered experience of the use of the described sampling train. This configuration is the standard configuration. One of the project partners has gained experience with an alternative configuration which is described in Appendix 13.6.

5.6. Description of sampling Module 4 (volume metering)

Figure 5-6 displays the Module 4 equipment: a pump, a flow indicator, pressure and temperature measurement and a volume flow meter.

5.6.1. 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 1 m^3_n/h at an absolute pressure of 0.5 bar. 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 1 bar. However, for slightly overpressurised gasification systems (up to 1,5 bar) a pump might still be needed.

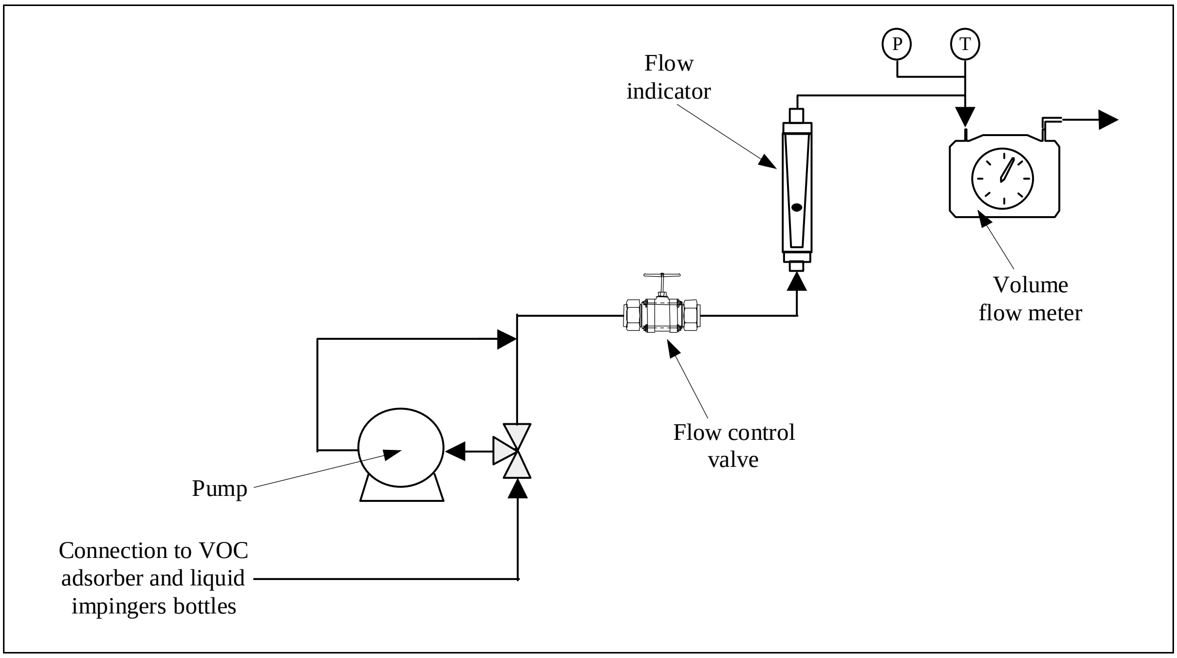

Figure 5-6: Pump and flow measuring equipment in Module 4.

5.6.2. Sample gas meter

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

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

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

5.7. 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 5-2. 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 fulfil the required national safety regulation for potentially explosive atmospheres (e.g. standard EN-50014).

Table 5-2: 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
	Ice bath
	Compression cooler
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
Backup VOC adsorber	e.g. activated carbon, XAD or Tenax
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
	Salt, Ice
Sample bottles:	500 ml storage bottle with PTFE coated screw plug (GL45) and pouring ring
Gaskets in the filter holder etc.	PTFE or graphite or copper or Viton

5.8. Design operating conditions for the sampling train

The design sample gas flow rate of the solvent impingement sampling train is 0.1 – 0.6 m^3_n/h whereas the minimum absolute pressure in the sampling duct is 0.6 bar.

The volume of the gas sampled depends on the tar content of the gas. The recommended minimal sampling volume is 0.1 m_n^3 for all producer gas types. The total content of tar in the solution should be at least 100 mg/kg for gravimetric analysis and about 10 mg/kg (10 ppm) of solution for each compound analysed by GC. However, the GC detection limit is significantly lower for single components (0.25 ppm).

The sample probe temperature in updraft gasifiers is maintained between 100 and 125°C and in downdraft and fluidised-bed gasification at 300-350°C.

The temperature of the particle filter varies with the gasifier type. When sampling high temperature tar from downdraft and fluidised bed gasifiers, the preferable filter temperature is 300-350°C or higher in order to avoid condensation of tar on carbon rich particles. When sampling low temperature tar from updraft gasifiers the filter temperature is 100°C to avoid polymerisation of the tar.

At filter temperatures above 250°C, Viton gaskets or plate rings made of copper can be used for the filter housings sealing. At temperatures below 250°C, PTFE can be used.

5.9. Site specific sampling train set-ups

The application of a sampling procedure is dependent on the gasifier type. Most of the gasifiers fall in four categories, which are: 1) fixed-bed updraft, 2) fixed-bed down-draft, 3) fluidised-bed and 4) entrained-flow. In the Appendix 13.1 (Figure 13-1), the basic principles of these gasifier types and typical operating behaviour are shown.

Tar concentrations and its composition and particle concentration depends on the gasifier type and design, on the operating condition, feedstock etc. The tar concentration in countercurrent (updraft) gasifiers is usually high (typically 100 – 200 g/m^3_n) compared to other gasification applications (tar content usually under 20 g/m^3_n). Fluidised bed gasifiers typically produce the highest particle concentration.

Table 5-3 provides an overview of various site specific sampling train arrangements. The term ‘Raw Gas’ in the figure means gas collected direct from the gasifier without any gas cleaning. The term ‘Clean Gas’ in the figure means gas cleaned either catalytically, by scrubbing or physical methods (ceramic or bag filters etc).

Gasifier type	**Fixed bed cocurrent**		**Fixed bed countercurrent**		**FB / CFB atmospheric**		**FB / CFB pressurised**	
Sampling site	RawG	CleanG	RawG	CleanG	RawG	CleanG	RawG	CleanG
Module 1 (Gas conditioning)	X	X	X	X	X	X	X	X
Module 2 (Particle collection)	X	X	(X)	X	X	X	X	X
SubModule 3.1 (Moisture/tar condensation)	X	(X)	X	X	X	(X)	X	(X)
SubModule 3.2 (Tar/VOC collection)	X	X	X	X	X	X	X	X
SubModule 3.3 (Backup/guard filter)	X	(X)	X	X	X	(X)	X	(X)
SubModule 4.1 (Gas suction)	X	X	X	X	X	X	-	-
SubModule 4.2 (Volume integration)	X	X	X	X	X	X	X	X
SubModule 4.3 (Offgas handling)	X	X	X	X	X	X	X	X

Table 5-3: Overview of sampling train arrangements depending on gasifier type.

Remarks: X = Reference arrangement; (X) = site specific; - = not needed; RawG = Raw gas after gasification reactor (before gas cleaning); CleanG = Clean gas after gas cleaning.

The complete reference set-up of the isokinetic sampling train for tar and particles from biomass producer gases at ambient pressure is shown in Figure 5-7.

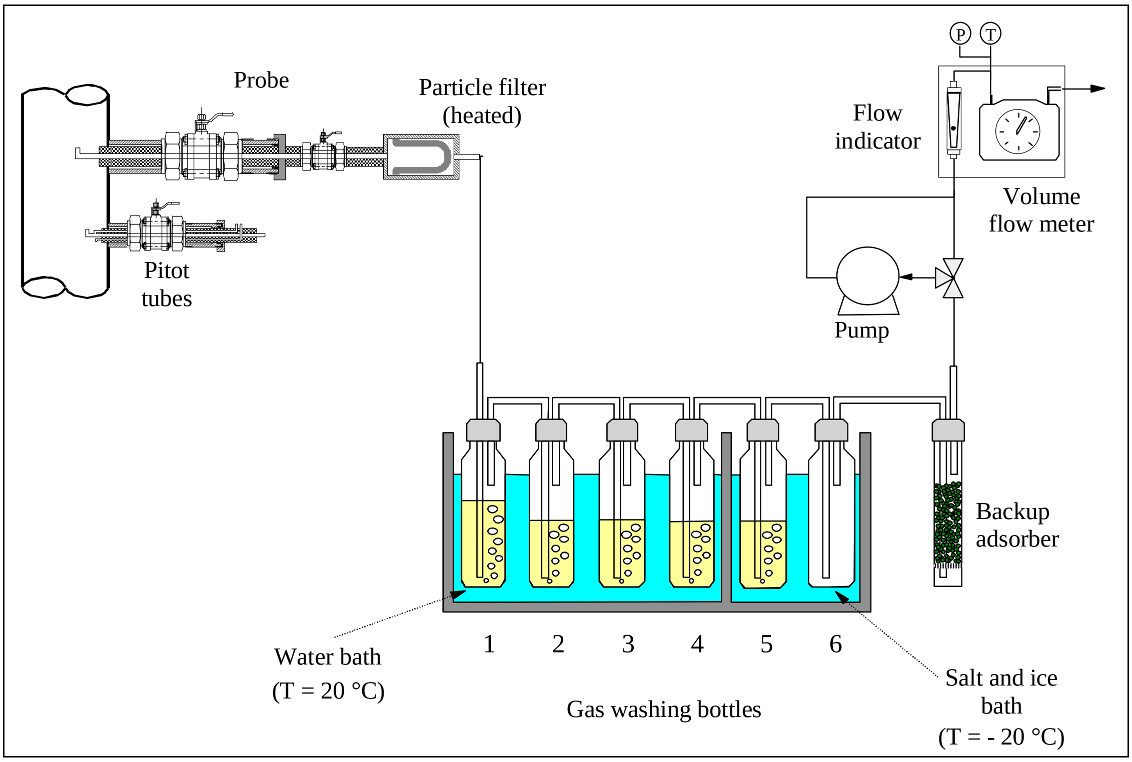

Figure 5-7: Atmospheric and isokinetic sampling train for tar and particles with removable probe and pitot tubes for flow measurement

Remarks: The set-up is based on the use of isopropanol as a tar collecting solvent; alternatively to the pitot tube, an O-type probe can be used for isokinetic measurement

5.10. Type of solvent used

The condensate and the organic compounds present in the producer gas are collected in a solvent. Direct condensation of the liquid effluent without a solvent as a diluting media can result in further reactions of the trapped compounds. The reactivity is suppressed by the solvent. Direct condensation of the effluent also causes that tar aerosols (which are formed when the producer gases cools down, i.e. in the moisture collector) will likely pass the condenser. The absorbing liquid captures these aerosols and the design of sampling train and the choice of the solvent has been optimised to perform this function.

The modular sampling train set-up displayed in Figure 5-1 to Figure 5-7 can be used for both water miscible and non-water miscible (non-polar) solvents.

The boiling point (evaporation rate) and the water solubility are the main parameters, which influence the sampling train set-up:

- With water miscible solvents exhibiting a medium volatility (like isopropanol), a liquid quench with the solvent can be used as an option for gases with high tar levels.
- With water miscible solvents exhibiting a high volatility (like acetone), the first impinger (kept at 0°C) after the condenser can not be filled with solvent. Also the liquid quench option with the solvent cannot be used. Instead conventional cooling (with heat exchangers) or a liquid quench with water can be used.
- With non-polar solvents (like iso-octane) a liquid quench with the solvent cannot be used (at least two-phase liquids or even formation of emulsions occurs). Instead conventional cooling (with heat exchangers) or a liquid quench with water can be used. Besides, attention should be paid to possible formation of ice on the tip of (small) impinger tubes.

In this Guideline isopropanol has been selected to be the most appropriate solvent. The R&D that was performed to come to this selection is described elsewhere (Neeft, Knoef, Zielke, Sjöström, Hasler, Simell, Dorrington, Abatzoglou, Deutch, Greil, Buffinga, Brage, Suomalainen, 2001).

6. Planning and preparation of sampling

6.1. Requirements for the plant operating conditions

Measurements should be performed during stable and known operating conditions of the gasifier. The characteristic operating conditions (such as heat rate, gas production rate, fuel type) during the sampling are summarised together with the plant specification in the sampling logs (Chapter 13.7.4).

6.2. Requirements for the main gas stream

The flow in the main gas duct must be undisturbed for ideal isokinetic sampling. The measuring port(s) should not be positioned in bends or near ventilators, valves etc. As a general rule, the length of the main gas duct before the sampling port should be at least 5 times its hydraulic diameter D and at least 3 times its hydraulic diameter after the sampling port (ISO9096 or VDI2066, part 1). The number of sampling points at one port depends of the diameter of the gas pipe. The instruction to calculate the number of sampling points is given in ISO 9096 or in VDI 2066 (part 1).

Preferentially the main duct is in a vertical position for the mounting of the sampling port. The gas velocities in the main gas duct should be higher than 5 m/s.

6.3. Requirements for 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 3 mm. The sample nozzle diameter can be calculated with the equations given in Paragraph 7.1. The minimal nozzle diameter is 4 mm according to ISO 9096 and 5 mm according to VDI 2066, part 2. In this Guideline, the nozzle diameter should at least be 4 mm. Design parameters for nozzle shapes used to isokinetic measurements can be found in ISO 9096 or VDI 2066.

The sample probe is positioned in the same direction as the flow or positioned at a 90° angle to it. The sampling line is heat-traced at a constant temperature over the filter. The probe is maintained at the process temperature, but above tar condensing temperature, so as to prevent any condensation in the probe. 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, special material such as Inconel is preferred. The temperature of stainless steel sampling probe (AISI 310, AISI 316) should be limited to below 700°C preventing changes to the concentrations of tar compounds.

To avoid particle deposition in the sampling tubes, the gas velocity in the tubes must be higher than 25 m/s. The temperature of the tube must be 300 - 350°C to prevent the particles adhering to tar condensed on the tube walls.

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

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

6.3.1. 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 Figure 6-2).

Gas velocities in producer gas streams at near ambient pressure are preferentially measured with (calibrated) pitot tubes. The instructions for using pitot tubes are given in ISO 9096, an example of the layout is given in Figure 6-1. Pitot tubes must be heated to process temperature, back-flushing facilities being advantageous.

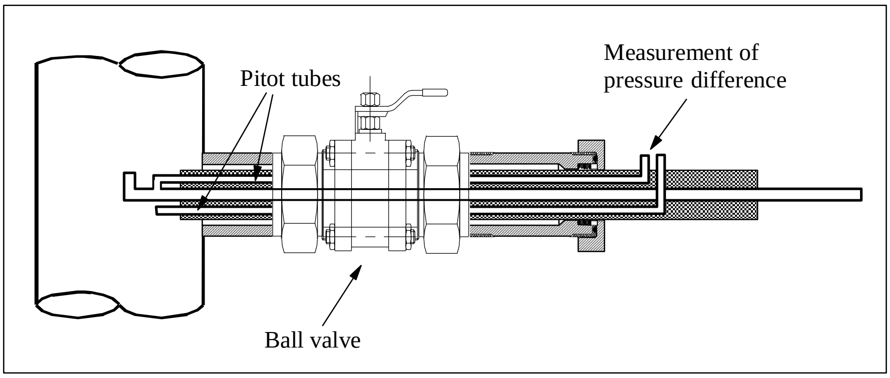

Figure 6-1: Pitot tubes for measurement of the producer gas flow.

In pressurised gasification applications removable pitot tubes cannot be used and hence gas velocities at the probe tip can not be measured. Alternatively, an O-type probe has been found to work well for pressurised producer gases (Figure 6-2). The O-type probe is also suitable for atmospheric applications.

If there is no velocity meter available calculation is performed according to Paragraph 7.1.

6.3.2. O-type probe for isokinetic sampling

Isokinetic sampling can be performed using an O-type probe configuration (Figure 6-2) 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.

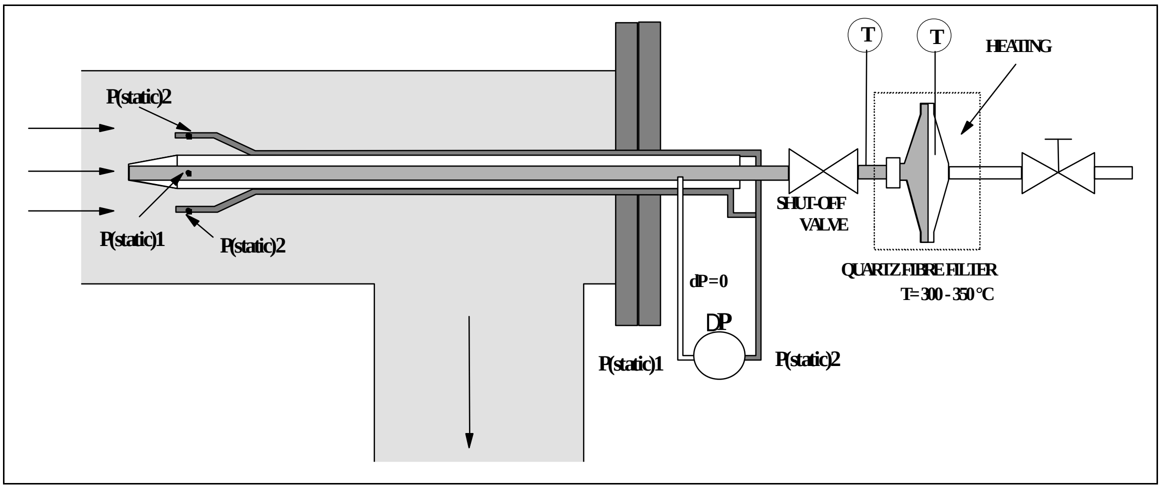

Figure 6-2 The configuration of the O-type probe

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.

6.4. Requirements for the sampling port

Sufficient space must be available to ensure easy access to sampling ports and placement of sampling equipment, typically an area of 4 m^2. There should be good air-conditioning 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 6-2) or other sampling probe(s) must be mounted before the start-up of the plant. The nitrogen flush through the probe tip has to 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 6-3. The sampling port includes a main shut-off valve (a 2” ball valve) which must be assembled before plant startup. 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.

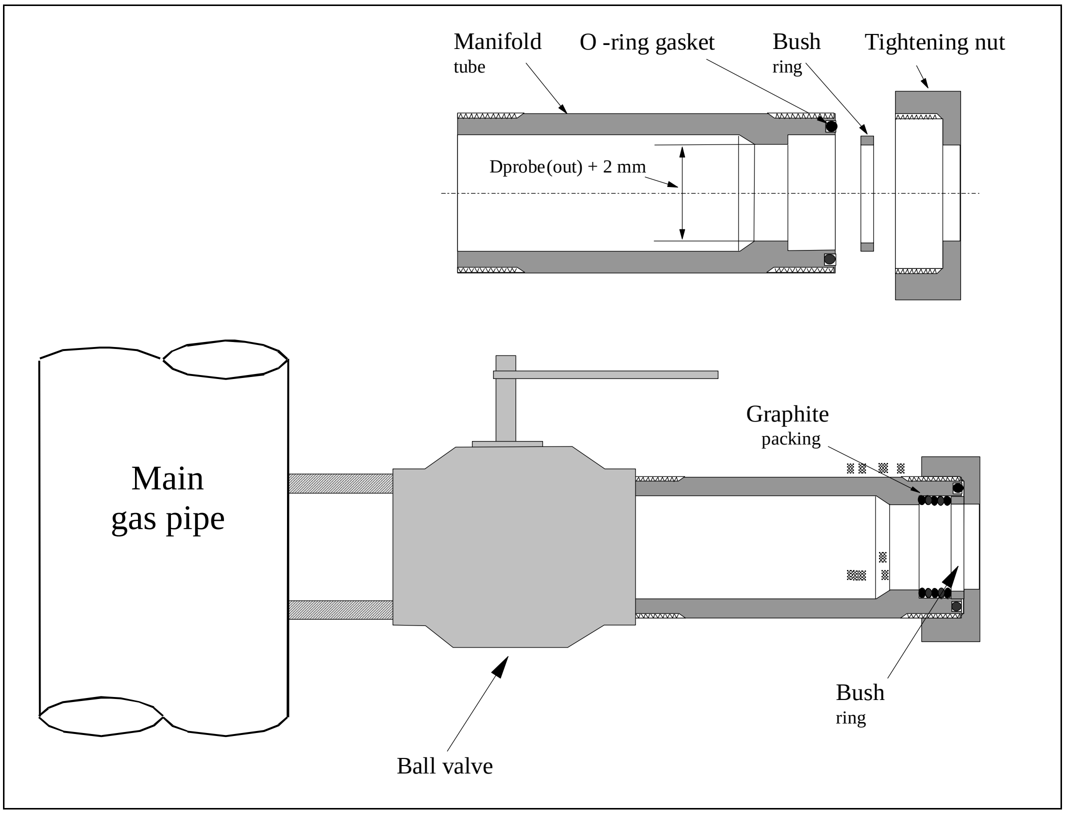

Figure 6-3: Sampling port with lock consisting of ball valve and stuffing box (the sampling probe is not shown)

6.5. Preparation of the sampling

6.5.1. Gas velocity meter

The pitot tube is the only measurement principle described within this Guideline 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 asks for 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.

6.5.2. Particle filter

Filter thimbles or plates must be preconditioned according to Paragraph 8.1.2. 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.

6.5.3. Moisture collector

Prior to sampling the moisture collector cooling 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 case where a liquid quench system is used, the recirculating system is filled with the chosen liquid. After that, the liquid pump is switched off.

6.5.4. Tar impingers

The solvent used for tar absorption and the (optional) glass beads used for improving heat and mass transfer are added in gas impinger bottles. In each impinger, approximately 50 ml of solvent is added. The drop-collecting bottle is placed after the impingers. The entire impinger train (incl. drop separator) is placed in the salt/ice bath. For a sampling temperature of –20°C, this cooling procedure requires approximately 30 minutes.

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, make sure that the mixture is wet.

6.5.5. Cleaning of equipment before site measurements

Before using the equipment in connection with a site measurement, all glass equipment (sampling probe, impinger bottles, fritts, transport bottles etc.) have to be cleaned according to an internal laboratory instruction. Oil or tar contaminated glass equipment have to be put to soak in an alkaline bath (pH 11-12) for 24 hours. After this the glass parts have to be washed in a laboratory dishwasher with the following program:

1. Primary rinse with soften water
2. Wash at 85 °C for 45 minutes.
3. Rinse 4 times with demineralizated water.

After this, the glass parts are 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 are sealed with plastic wrap (parafilm).

PTFE hosing has to be rinsed with DCM and acetone under save laboratory conditions until the tubes appear clean. From time to time, the cleaning procedure is checked by analysis of rinsing liquid. After washing, the tubes are sealed with plastic wrap (parafilm).

6.5.6. Choice of correct nozzle size

The diameter of the sampling nozzle is normally determined by the requirement that the isokinetic sample flow in the beginning of a measurement should equal to about 70% of the sampling trains pump capacity. In this Guideline the sample flow rate is limited to 0.1-0.6 m^3_n/h. The calculation of the correct nozzle size appears from Paragraph 7.1.

6.5.7. Backup VOC adsorber

The backup VOC sampler is positioned as specified and prepared according the type of adsorbens selected.

6.5.8. 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.

7. Sampling procedures

7.1. Isokinetic sampling

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

$$v'_a = v'_N \qquad \text{(Eq. 7-1)}$$

When the sample gas velocity n'_N is higher than the gas velocity in the duct n'_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 to be conducted within the following limits

$$0.95 < \frac{v'_N}{v'_a} < 1.15 \qquad \text{(Eq. 7-2)}$$

Within this Guideline, 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

7.1.1. 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

$$v'_a = \sqrt{\frac{2\cdot\Delta p_{Pt}}{r'_a}} = \frac{q'_{Va}}{A\cdot 3600} \qquad \text{(Eq. 7-3)}$$

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

$$v'_N = \frac{q'_{VN}}{a\cdot 3600} = \frac{q_{Vg}}{a\cdot 3600}\cdot\frac{p_{am}+p_g}{p_{am}+p_a}\cdot\frac{273.15+\Theta_a}{273.15+\Theta_g}\cdot\left(1+\frac{f_n}{0.804}\right) \qquad \text{(Eq. 7-4)}$$

From equations 7-1, 7-3 and 7-4 it follows that the volumetric gas flow rate through the gas meter becomes

$$q_{Vg} = \sqrt{\Delta p_{Pt}}\cdot 3600\, a\cdot\sqrt{\frac{2}{r'_a}}\cdot\frac{p_{am}+p_a}{p_{am}+p_g}\cdot\frac{273.15+\Theta_g}{273.15+\Theta_a}\cdot\frac{1}{(1+\frac{f_n}{0.804})} \qquad \text{(Eq. 7-5)}$$

7.1.2. 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 7-2 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 7-1.

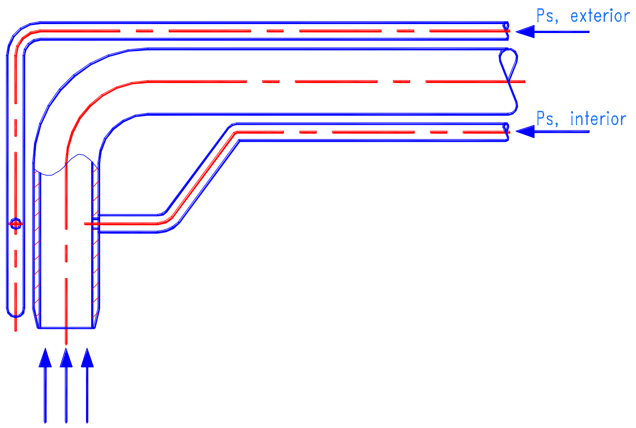

Figure 7-1 Simple O-type probe

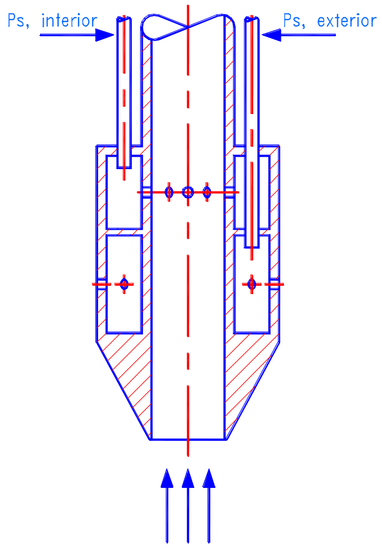

Figure 7-2 O-type probe

Isokinetic sampling conditions are achieved by equalising the interior and exterior static pressure signal. 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.

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 5 m/s, a 40% sampling error may result from a 12 Pa deviation from zero. For a gas velocity of 15 m/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.

7.1.3. Estimation of isokinetic sampling based on calculation from the gasifier load

Where pitot tubes or O-type probes can not be used or are not available, the producer gas flow rate and the isokinetic sampling rate can be calculated from a mass balance. The method presented here determines the producer gas flow rate from the gas yield and the gasifier load and can be applied to all types of gasifiers.

The calculation 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) are 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

$$q_{m,\,fuel}\,cc_{fuel} + \sum q_{V,agent}\,cc_{agent} \;=\; q_{V,gas} \cdot \left(cc_{gas} + c_{tar}\,cc_{tar} + c_{particles}\,cc_{particles}\right) + q_{m,\,ash}\,cc_{ash} \qquad \text{(Eq. 7-6)}$$

with $q_{m,\,fuel}$ = 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. Dividing equation by the fuel feeding rate and rearrangement gives the specific producer gas yield

$$Y_{gas} = \frac{q_{V,gas}}{q_{m,fuel}} = \frac{cc_{fuel} - c_{ash,fuel}\ cc_{ash}}{cc_{gas} + c_{tar}\ cc_{tar} + c_{particles}\ cc_{particles}} \qquad \text{(Eq. 7-7)}$$

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

The method determines the dry 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 (dry basis; 0°C, 101300 Pa). 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. 7-7) 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 Table 7-1.

		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 in particles	wt%	80	80	80
Tar	mg/m^3_n	100,000	1,000	20,000
C in tar	wt%	60	90	90
Gas yield according to (Eq. 7-7) Y_{gas}	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 7-1 Calculated producer gas yields from various gasifiers using wood as fuel

> Remarks: A survey of typical gas composition, tar and particle concentration from various gasifier reactor types is given in Appendix 13.1. Carbon content of the fuel is 49 wt% (typical for leavy wood); carbon content in particles, bottom ash and tar are estimated from typical experimental data.

For a typical cocurrent 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 countercurrent 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 (pre) information of 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 cocurrent gasifiers coupled to IC engines is based on the determination of the displaced gas volumes within the engine cylinders [BTG, 2000 and Ramackers, 1985]. This method requires the cylinder volume, the engine speed and air supply and the oxygen content in the exhaust gas.

7.1.4. 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 3 l/min for impinger bottles with frits. A specially designed VTT impinger is suitable in the range of 2 to 10 l/min.

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

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

$$\mathrm{n}'_N \cdot a \cdot 3600 \quad = \quad q'_{VN} \quad = \quad q_{Vg}\ (1+\frac{f_n}{0.804}) \cdot \frac{p_{am}+p_g}{p_{am}+p_a} \cdot \frac{273.15+\Theta_a}{273.15+\Theta_g} \qquad \text{(Eq. 7-8)}$$

the nozzle face area *a*

$$a \quad = \quad A \cdot \frac{q_{Vg}}{q'_{Va}}\ (1+\frac{f_n}{0.804}) \cdot \frac{p_{am}+p_g}{p_{am}+p_a} \cdot \frac{273.15+\Theta_a}{273.15+\Theta_g} \qquad \text{(Eq. 7-9)}$$

where $0.1 \le q_{Vg} \le 0.6$ $\mathrm{m}^3_{\mathrm{n}}$/h and the nozzle diameter d_N is calculated as follows

$$d_N \quad = \quad \sqrt{\frac{4 \cdot a}{\mathrm{p}}} \qquad \text{(Eq. 7-10)}$$

A general expression for calculation of nozzle diameter based on the assumption of a gas yield shown in Table 7-1 appears from the following equation:

With a gas yield value from Table 7-1, which fits the present object, it is possible to calculate the wet producer gas flow q'_{Va} and the gas velocity v'_a

$$q'_{Va} \quad = \quad Y_{gas} \cdot \dot{m}_{fuel} \cdot \frac{101300 \cdot (273.15+\Theta_a)}{273.15 \cdot (p_{am}+p_a)} \cdot (1+\frac{f_n}{0.804}) \qquad \text{(Eq. 7-11)}$$

$$v'_a = \frac{q'_{Va}}{A \cdot 3600} \qquad \text{(Eq. 7-12)}$$

The appropriate nozzle area is expressed by

$$a = A \cdot \frac{q'_{Vg}}{q'_{Va}} = A \cdot \frac{q_{Vg} \cdot (1 + \frac{f_n}{0.804})}{q'_{Va}} = A \cdot \frac{q_{Vg} \cdot 273.15 \cdot (p_{am} + p_a)}{Y_{gas} \cdot \dot{m}_{fuel} \cdot 101300 \cdot (273.15 + \Theta_a)} \qquad \text{(Eq. 7-13)}$$

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

7.2. Sampling train leak test

Leaking of the sampling train can be tested either by pressurising or underpressurising 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 0.2 bar above or below the maximum sampling over or under pressure.

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 leak indicators. Stopping the gas supply from the cylinder and carefully opening the shutoff valves after the pump terminates the leakage test. The pressure release procedure must be undertaken with utmost care and generally lasts 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 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 penetrate the condenser and the impingers, 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 generally lasts for at least one minute.

If the gas mixture to be studied does not contain oxygen, leaks can be detected also during sampling by an oxygen analyser connected to the sampling line.

7.3. Execution of sampling

It is preferred that the gas composition, the gas temperature and the static pressure in the gas line are measured and recorded continuously.

The leak test of the sampling train (see Paragraph 7.2) must be made before the probe and the particle filter are mounted.

The sampling apparatus for atmospheric gasifiers is designed such that the probe can be inserted and removed from the sampling port during gasifier operation without any gas leaks or entry of air into the gas line. The probe is inserted via the sampling port to the closed shut-off valve. The procedure is as follows:

1. Ensure that the sampling port is free from tar and particle deposits between the ball valve and the gas line. Ensure that the ball valve can be operated easily and that the stuffing box can be tightened.
2. Ensure that the impinger train is connected correctly and that the stop valve in the sample line is closed. Mark the distance from the sampling point to the stuffing box on the sampling probe. Insert the probe into the lock and tighten the stuffing box slightly. Heat the sampling probe to its set value and cool the impinger bath to its set value.
3. Impurities must not enter the nozzle opening during insertion and withdrawing of the probe. Do not touch any walls with the nozzle opening.
4. Open the ball valve and move the heated probe forward into sampling position (normally one point in the centre of the gas line is sufficient in gas lines with a diameter smaller than (or equal to) 350 mm). In gas lines with a larger diameter, the number of sampling points have to be determined according to ISO 9096. The nozzle axis is held at a right angle to the gas flow direction. Tighten the stuffing box.
5. Mount the particle filter and heat to its set value.

6. Wait for the correct sampling temperature.
7. Read the gas volume meter. Record the starting time. Turn the probe tube until the nozzle faces directly upstream, start the vacuum pump, start the timing device and open the stop valve. Then adjust the control valve to give the required flow reading as calculated according to nozzle size, gas velocity, etc.
8. Monitor the rotameter, which is used as a indicator of the gas flow and the static pressure measurement at the gas volume meter. Adjust the control valve as necessary throughout the sampling period to maintain isokinetic sampling. Record the temperature and static pressure at the gas volume meter at regular intervals. During sampling check the temperature of the impinger cooling bath and the temperature of the filter housing.
9. Occasionally agitate the condenser cooling liquid and the impingers to ensure even temperature distribution in the cooling media.
10. When an adequate quantity of tar and particles has been collected or if the pressure drop in the sampling train prevents isokinetic sampling, the sampling has to be terminated (see Paragraph 7.4).
11. Close the stop valve in the sample line, stop the timing device, stop the vacuum pump and turn the probe tube through 90 °. Dismantle the particle filter. Withdraw the probe until the ball valve can be closed and then remove the probe with great care in order to avoid contact with any deposits within the gas line or the sampling port.
12. Record the time for stopping and the gas volume meter; as soon as possible remove the filter cartridge from the filter housing and store it in solvent in a tightly closed bottle, to avoid polymerisation of tar during cooling. Then clean the sample line (see paragraph 7.5) and prepare the samples for subsequent analysis (see paragraph 7.6).
13. When the probe is not removed (e.g. press. gasifiers), the probe is flushed with N_2.

When it is necessary to repeat the measurements of the tar and particle concentration, then repeat procedures 1 to 13. Prepare the next sampling (including leakage test) as soon as possible and be sure that comparable plant conditions are available. Normally, between 2 and 6 measurements should be sufficient for determination of tar and particle content in producer gas. If the gasification process is not quite stable, it could be necessary to carry out even more measurements.

7.4. Duration of sampling

The actual quantity that is collected depends on the concentration, sampling time and pump capacity. For low concentrations, increased sampling time and pump capacity will be needed in order to collect an adequate quantity. Otherwise, improvement of the weighing procedure is necessary to obtain an acceptable weighing error.

With gravimetric measurements of tar and particle concentrations it is assumed that the weighing inaccuracy is better than 5%. To achieve this, an adequate quantity of tar and particle matter has to be collected. With an error of 0.2 mg per weighing, and considering the fact that the collected amount is calculated from the difference of two weightings (5% $\cong$ 0.3 mg), an adequate quantity of gravimetric tar in the sample for the analysis amounts to about 6 mg.

For GC based individual compound analysis, the adequate compound quantity amounts to about 5 to 10 mg/litre solution. The sampling duration can be calculated on the basis that 300 ml solvent is used for sampling and equipment cleaning and 300 ml of solvent is used for the Soxhlet extraction procedure from the particle filter. In case where the optional liquid quench system is used, an additional amount of approx. 300 ml of solution will be generated.

In connection with high concentration measurements the minimum sampling time for collection of an adequate quantity of matter can be < 30 minutes. In this case it is recommended to sample more matter than the minimum matter required. If the particle filter clog up within 30 minutes, it is recommended to stop the measurement and start a new measurement with smaller nozzle and lower sample flow rate, but still in accordance with isokinetic sampling.

In connection with low concentration measurements it is recommended to use the largest nozzle possible and the highest allowed sampling flow rate, also in accordance with isokinetic sampling.

With high moist gas, a large amount of condensate will be generated thus requiring adequate volumes of condensers. Generally, also the moisture content of the gas is determined thus a certain amount of condensate is required to accurately determine the gas moisture.

7.5. Equipment cleaning after sampling

After termination of sampling, the unheated parts of the sampling train must be rinsed in order to collect tar deposits from the train. Disconnect the flexible tubing from the probe tube. With a wash bottle inject solvent into the hose and shake until the hose appears clean. Use no more solvent than necessary. Transfer the rinsing solvents to a storage bottle.

7.6. On-site preparation and storage of samples for analysis

The sampling solution is stored in a sealed, dark bottle, which is marked with a clear identification label and kept at a temperature < 5 °C until analysis. In some cases (e.g. countercurrent raw gases) it may be necessary to store the liquids in nitrogen atmosphere and in dark bottles. The analysis is preferably performed as soon as possible and should be completed within a month after sampling. Instead of a dark bottle, also a glass bottle can be used that is kept in the dark.

The particle filter must be handled with great care. When removing the filter from the housing it is imperative that no particles are added to or dropped from the filter. It is also imperative that no filter material is lost during handling.

The filter cartridge is stored in solvent in a jar with sealed screw cap. At least the same solvent must be used for the filter storage as for the Soxhlet extraction, preferably the same solvent as for sampling and/or for analysis). The storage jar is marked with a clear identification label and it is kept at a temperature < 5 °C until analysis.

The plate or membrane filters are stored in a sealed Petri dish with a suitable diameter.

8. Analysis of samples

Biomass tar is a complex material consisting of hundreds of compounds, varying widely in polarity and molecular mass. The main products from the thermal processing of biomass are carbon monoxide, carbon dioxide, hydrogen and methane. However, small amounts of organic 'contaminants' are formed as undesirable by-products and it is a common perception that these toxic by-products will have detrimental effects both on down-stream treatment plant and power generation packs, and if emitted to atmosphere, the local environment. Reliable sampling and analysis of these products from biomass gasification is essential for the successful process development and economical operation of commercial gasifiers.

During the tar formation period in the gasifier the free radical content is high rendering the tar mixture unstable and reactive. When the tar is isolated and allowed to cool down polymerisation/oxidation reactions occur resulting in a high molecular weight material with complex structures. The analysis of the tar should be performed as soon as possible after sampling but within one month, minimising any polymerisation/oxidation reactions.

Positive identification of the condensed material as biomass tar is performed using GC-MS, which is used to identify the compounds present in the tar. The presence of tar is indicated typically by the presence of the US-EPA suite of PAH compounds, phenols and BTX. Quantitative determination of each compound can then be performed either by GC-MS or GC-FID analysis using internal standards. It may be necessary for the process operator to quantify certain compounds present in the tar and to use these as markers in order to improve the gasification process.

Not all of the tar constituents are amenable to GC analysis, because of the presence of high molecular weight material. GC analysis will usually determine more than 80% of the tar, the remainder being high molecular weight material of >350 g/mol. Only for updraft gasifier tars, this fraction can be considerably lower.

The main compounds of interest to operators, particularly of gas turbines, are the PAH compounds in the range naphthalene to indeno (1,2,3 cd) pyrene, phenols, methylphenols and dimethylphenols.

Figure 8.1 shows schematic for post sampling procedures

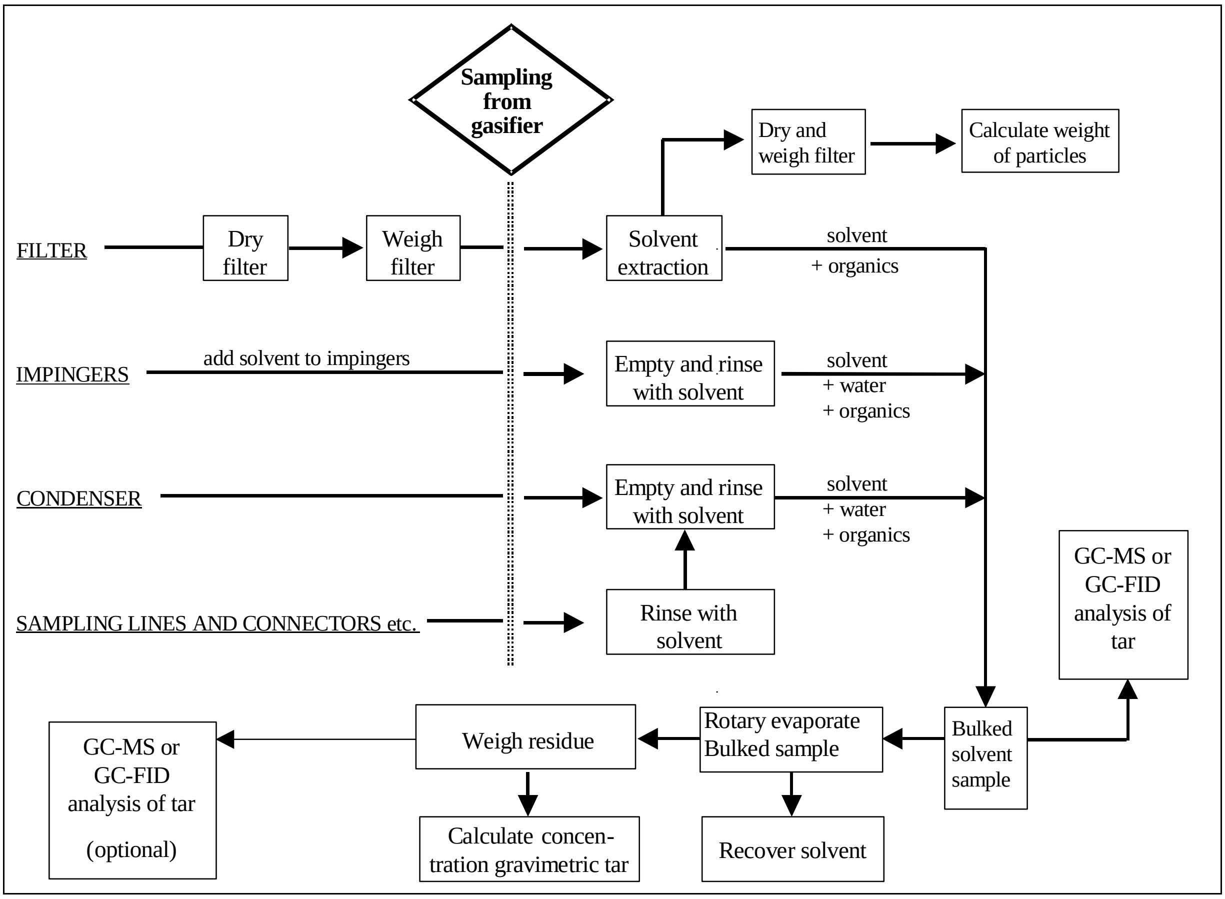

Figure 8.1 Schematic Showing Post Sampling Procedures

8.1. Gravimetric analysis

This procedure is based on conventional and well-proven methods for the gravimetric determination of both solid particles and organic species. Equipment utilised in this Guideline is available in most analytical laboratories.

8.1.1. Equipment for gravimetric analysis

Main items:
Soxhlet apparatus, standard rotary evaporator with pressure indicator, desiccator.
Calibrated analytical balance, accuracy 0.1mg.

8.1.2. Preparation of particle filter

Note: plate filters are recommended for particle concentrations of less than 20 mg/m_n^3 and thimble filters for concentrations greater than 20 mg/m_n^3. See section 5.4. When a plate filter is used, the determination of particle concentrations is less accurate or might prove impossible.

i. Dry the quartz thimble or plate filter in an oven at 110°C at atmospheric pressure overnight (according to ISO 9096).

ii. Allow to acclimatise in a desiccator at room temperature. Weigh the filter using an analytical balance with an accuracy of ± 0.1 mg.

iii. After sampling and extraction, the same weighing procedure is followed to determine the particle content.

iv. Calculate the mass of particulate material collected as described in Chapter 9.

8.1.3. Soxhlet extraction procedure

i. Open the filter housing and transfer the thimble or plate filter to the Soxhlet apparatus. Keep it in the vertical position to avoid loss of particles. To avoid polymerisation of tar this procedure should be undertaken immediately after finishing the sampling, when the filter is still hot. Carefully add the appropriate amount (250-500 ml) of isopropanol to the Soxhlet apparatus. Extract the filter until the isopropanol is clear, but at least overnight.

i. Remove the filter from the Soxhlet and keep in the vertical position.

ii. Dry the extracted filter thimble at 110°C at atmospheric pressure overnight.

iii. The amount of particulate matter is determined by weighing the dry/washed filter cartridge. The same drying method described for the clean filter must be used. The weight of particles is determined by difference. The concentration of particles in the producer gas can be calculated in mg per normal cubic metre (mg/m_n^3) using the volume of gas sampled, the temperature and pressure readings, as described Chapter 9.

iv. For quality control purposes an unused ‘blank’ filter can be run in parallel to the used filter. This will ensure that there are no error contributing factors from the Soxhlet procedure.

8.1.4. Determination of gravimetric tar mass

Isopropanol from the filter extraction procedure (Section 8.1.3) is bulked with the isopropanol solution collected from the impingers and condenser. The mass of gravimetric tar is determined by means of solvent distillation and evaporation. The recommended procedure for evaporation of the isopropanol tar solution is as follows:

i. Using a standard rotary evaporator with a pressure indicator. Adjust the flow rate of water to reach a vacuum of 100 mbar with an empty flask.

ii. Use a 200 or 250 ml flask and acclimatise it for at least 5 minutes at a specific site in the lab. Then, weigh it with an accuracy of 1 mg or preferably 0.1 mg. Pour about 100 ml of the tar solution in the flask. Weigh the flask again to determine the weight of the solution.

iii. Connect the flask to the rotary evaporator and start the evaporation with the water bath at 55°C. The pressure will be higher than 100 mbar at the start and will gradually fall to 100 mbar. Drops should fall from the cold finger at a rate of 1-2 drops per second. Once almost all solvent is evaporated, the rate of drops falling will decrease. With a stopwatch observe the time between two drops falling. Continue until there are at least four (4) seconds between two consecutive drops falling.

iv. After the latter of these two drops, continue the evaporation for a further fifteen (15) more minutes. If at this point traces of water are observed, add 20 ml of ethanol and restart at step (ii.). If no traces of water are observed, continue the evaporation for another thirty (30) more minutes while the sample is flushed with nitrogen. Adjust the nitrogen flow so that the vacuum pressure does not exceed 350 mbar.

v. Remove the vacuum by letting in air and shutting off the nitrogen purge. Then stop the rotation of the flask, remove the flask from the heated water bath and dry it. Give the flask and tar at least 5 minutes to acclimatise at the same location as in step (i.). Then, weigh the flask accurately and calculate the amount of gravimetric tar as described in Section 9.

vi. To determine the GC-detectable components in the gravimetric tars (which is optional) re-dissolve the tars as described in Section 8.2.5 and perform a GC analysis.

8.2. Gas chromatographic analysis

The gas chromatographic analysis techniques described in this section are based on standard analytical methods used for the detection of aromatic hydrocarbons. Quantitative analysis by GC-FID and GC-MS is described in this section, although qualitative GC analysis can be useful for ‘finger-printing’ compounds in the sample. Addition of an internal standard is useful to estimate semi-quantitatively the composition of the tar. If an internal standard is not used then no estimation of the proportion of components can be undertaken. Chromatographic data obtained by GC-FID will not be as detailed as that obtained by GC-MS.

8.2.1. Gas chromatographic equipment and columns

Main items:

Gas Chromatograph-Mass Spectrometer (GC-MS)
Gas Chromatograph – Flame Ionisation Detector (GC-FID)
Column – non-polar capillary GC column (5% diphenyl-95% polysiloxane)
Analytical balance (accuracy 0.1mg)*
Volumetric flask*
Syringe*
Pipette*

* calibrated to relevant National Standards

8.2.2. Operating conditions of gas chromatographs

The chromatographic equipment and operating parameters employed will ultimately depend on the physical and chemical characteristics of the solvent used to dissolve the tar sample. Operating parameters described are generalised and may need to be modified to accommodate the requirements of the selected analyser used (GC-MS or GC-FID) and the type of column fitted.

Typical equipment required for GC-MS and GC-FID analysis of tar solutions:

GC column	for example DPDM-siloxane (5%diphenyl + 95% dimethyl) copolymer phase typically: 30 to 60 m length, 0.25 mm id., film thickness 0.25 µm (The column is conditioned using the following temperature programme: 30°C up to 300°C at a rate of 3°C min^{-1} with a final hold temperature of 1 hour)
High resolution gas chromatograph	
Bench top mass spectrometer with mass range of 20-400 g/mol.	
Integration software package (usually included with MS)	
Carrier gas:	Helium

Linear velocity of carrier gas: typically 31.6 cm/s (or to suit system selected)
Pressure: typically 80 kPa
Flow rate of carrier gas: 1-2 cm^3/min
Split ratio: typically 75:1 (ratio depends on sensitivity of instrumentation and sample concentration)
Injection volume: typically 1 to 5μl
Oven programming: Initial isothermal at 50°C for 5 minutes
Temperature programme at heating rate of 8°C min^{-1} up to 250°C
Total run time 30 minutes
Injector temperature: 250°C

8.2.3. Quantitative GC-MS analysis

8.2.3.1. Preparation of Internal Standard (ISTD)

Internal standard solutions are prepared from pure standard materials and are prepared in dichloromethane, although isopropanol is often preferred on health and safety considerations. If the standard is a suspected carcinogen, primary dilutions of this material must be undertaken in a fume cupboard. For GC-MS analysis the recommended internal standard suite of compounds is phenanthrene-d$_{10}$., benzene-d$_8$, phenol-d$_6$, or benzopyrene-d$_{12}$.

i. A small amount of solvent is placed at the bottom of a ground glass stoppered volumetric flask. The solvent is the same as the solvent used in the sampling procedure, which is isopropanol.

ii. Each compound is weighed in its own decanter in the following way (getting solid compounds into a volumetric flask is difficult without loosing some part of solids for instance on the surface of the flask neck):
   - A small decanter is tared on the analytical balance;
   - A compound is weighed in the flask;
   - Solvent is poured into the decanter and the compound is dissolved;
   - Dissolved compound is poured into the volumetric flask;
   - The decanter is rinsed and the rinsing solvent is also poured to the flask;

   The lightest model substances, being readily volatile, should be treated quickly.

iii. Dilute to volume, stopper the flask, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microlitre from the net gain in weight.

iv. Transfer the ISTD solution into an amber teflon-sealed screw-cap bottle and store in a refrigerator. All standards must be replaced after six months or if comparison with check standards indicates a problem.

8.2.3.2. Preparation of calibration standards

Calibration standards are made up from pure compounds listed in Section 13.2 using the same procedure described for preparation of the ISTD (Section 8.2.3.1). The presence of tar is indicated typically by the presence of the US-EPA suite of PAH compounds, phenols and BTEX. The calibration standard should be made up using these compounds in order to quantify the level of each compounds present.

Organic compounds that are not included in the calibration standards list, or are not available can be reported semi-quantitatively by assuming a response factor of unity or taking an average response factor for type of compound.

Prepare calibration standards at between two and five concentration levels for each compound of interest. A calibration file can now be set up using both the calibration and internal standard solutions. The operating parameters and conditions for quantitative GC-MS analysis are the same as those described for qualitative GC-MS analysis.

8.2.4. Quantitative GC-FID analysis

A GC-FID quantitative analysis is also possible as an alternative using a similar procedure to that described for quantitative GC-MS analysis. It should be noted however, that the identification of compounds is not absolute because compounds are identified by retention time only, which can lead to compounds with similar retention times being wrongly identified.

8.2.4.1. Preparation of Internal Standards (ISTD)

As described in Section 8.2.3.1 for GC-MS analysis, but use n-dodecane made up accurately to about 100-500 ng/µl as the internal standard.

8.2.4.2. Preparation of calibration standards

As described in Section 8.2.3.2 for GC-MS analysis.

8.2.5. GC–MS and GC-FID analysis procedures

8.2.5.1. Preparation of sample for GC-MS and GC-FID analysis

i Take 10 ml of the bulk sample solution (see Figure 8-1) and add 0.01 mg of ISTD solution. Depending on the concentration of tar, the sample can be diluted to ensure that the concentration of organic components fall within the detection limits of the instrument.

ii Shake contents of volumetric flask. Transfer the sample into an amber teflon-sealed screw-cap bottle and store in a refrigerator until ready to use.

iii All volumes and weights will vary depending on the levels of each compound present, and the type of biomass initially used.

Optionally, GC-FID or GC-MS analysis can also be performed with the tar residue from Section 8.1.4. Then, prepare the sample as follows:

i Accurately weigh about 0.1 g of the tar residue into a 10 ml ground glass stoppered volumetric flask. Depending on the concentration of tar, the sample can be diluted to ensure that the concentration of organic components fall within the detection limits of the instrument.

ii Add 0.01 g of ISTD solution, make up to the mark with dichoromethane and shake contents of volumetric flask. Transfer the sample into an amber teflon-sealed screw-cap bottle and store in a refrigerator until ready to use.

iii All volumes and weights will vary depending on the levels of each compound present, and the type of biomass initially used.

8.2.5.2. Analysis by GC-MS or GC-FID

i Prior to analysis allow the sample to reach room temperature. Inject between 1 µl and 5 µl of the sample from Section 8.2.5.1 onto the GC column using a calibrated syringe. The volume injected will depend on tar concentration, and will be known from experience with analysis of each type of biomass tar.

ii The operation of the GC-MS and GC-FID systems will be dependent on the type of system used, the manufacturer’s instructions, the data processing system used, the column used etc.

8.2.5.3. Identification of compounds

This is based upon retention times in combination with mass spectra.

i **Identification by retention time.** The width of the retention time window entered in the software program and used to make identifications should be based upon measurement of actual retention time variation of standards. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

ii **Identification by mass spectrometry.** Set up the calibration software to search for the specified components based on their retention time and their mass spectrum. Identification of the compounds present in the total ion chromatogram is performed by comparison of the unknown spectra with the mass spectral library.

8.2.6 Calculation of GC results

The results are calculated as described in Chapter 9, in conjunction with the following equations.

The system software can be set up and used to automatically quantify the compounds analysed. Response factors can also be calculated manually using the following equation:

$$RF_c = \frac{A_c / A_{is}}{M_c / M_{is}}$$

where RF_c = Response factor for compound
A_c = Area of compound
A_{is} = Area of internal standard
M_c = Mass of compound
M_{is} = Mass of internal standard

The mass of each compound can be calculated using one of several methods:

i Automatically using the system software if an appropriate calibration file has been set up
ii Using a spreadsheet with response factors and manual input of peak areas
iii Manual calculations using response factors and peak areas:

$$M_c = \frac{A_c M_{is}}{A_{is} RF_c}$$

9. Calculation of results

9.1. Error calculation

9.1.1. Classification of errors

This chapter deals with error calculation and accuracy of measurement. In this context it is useful to make a few general remarks on the classification of errors.

Generally, errors can be divided in two categories: *systematic errors* and *accidental errors*.

Systematic errors are caused, for example, by wrong calibrations of measurement instruments, by poor measurements, by impurities in used chemicals or by unknown causes. The latter becomes clear only if results are compared with those of other researchers or other laboratories using different measuring devices and preferably other methods.

Accidental errors are unpredictable. They find their cause in physical noise, fluctuations by other causes and reading errors. Repeating of measurements will show a normal distribution around a certain average. From this the estimated error in the average can be determined.

In case of only a single experiment, the error has to be estimated. As an example, with a ruler length can be read with accuracy of ± 0.2 mm. The accuracy of good commercial measuring devices is normally - sometimes as an individual calibration report - indicated by the supplier. In general the maximum deviation is indicated, which may have a systematic character and is bigger than the mean accidental error.

Errors can be presented as an *absolute error* or *relative error*. *Absolute errors* have the same dimension as the measured quantity, a length for example can be presented as 21.3 ± 0.2 mm. *Relative errors* are given as a fraction of the measured quantity, or as a percentage. A relative error is a dimensionless number. For example 21.3 mm ± 1%.

9.1.2. Propagation of errors in the final result

Normally we are interested in the final result, being a function of one or more measured quantities. Here the issue is to find out how errors in the measured quantities carry over in the final result. As an example, the equilibrium constant K of a reaction is measured as K= 305 ± 5.What will the error be in the standard free enthalpy of reaction (at T=300 K): G= RTlnK=14.268 kJ/mol ?

The answer to this question can be found by differentiation:

If the error in x is equal to D *x, then the error* D *f in f(x) is equal to* $\Delta f = \left|\frac{df}{dx}\right| \Delta x$.

In this example the error in G is equal to -RTΔK/K=41 J/mol; The final result is thus written as G=14.27 ± 0.04 kJ/mol.

Note that normally, errors, indicated without any further note are always meant as the mean error or standard deviation σ. Due to the existence of different types of errors, the general abbreviation for 'error' used in this section is chosen to be Δ.

Where an error is built up of errors of more independent measured quantities, the different contributions should be summed. However, normal summing of errors is wrong: errors of different independent sources can be + or – en will partially compensate each other. Therefore, the right way of summing is to the square root of the sum of the quadratic individual errors:

If f=x+y, then $(\Delta f)^2 = (\Delta x)^2 + (\Delta y)^2$. In other words: independent errors sum quadratic. In general the error propagation law for f, a function of x,y,z,…. is[i]:

$$\Delta_f^2 = \left(\frac{\partial f}{\partial x}\right)^2 \Delta x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \Delta y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \Delta z^2 + \ldots\ldots\ldots \qquad \text{(Eq. 9-1)}$$

9.2. Sampled gas volume

The sampled producer gas volume V at normal conditions is the difference of the readings from the calibrated gas meter during the sampling procedure, corrected for the actual p and T of the sampled gas at the dry gas meter. As the gas temperature and pressure can increase or decrease during the sampling period, the exact calculation of the displaced gas volume would require continuous gas meter, temperature and pressure reading followed by fractional volume integration. Within this Guideline, a simplified equation is used which contains the difference in the gas meter reading between the start and finish of the sampling period, the mean gas meter temperature <T> and mean pressure <p> over the sampling period:

$$V = \left(V_{stop} - V_{start}\right) \cdot \frac{<p>}{P_0} \cdot \frac{T_0}{<T>} \quad [m_n^3] \pm \Delta V \qquad \text{(Eq. 9-2)}$$

, with P_0=101300 Pa and T_0=273.15 K and ΔV being the 'error' in V.

The best estimate of the average of N values of p or N values of T is given by:

$$<p> = \frac{1}{N}\sum_{i=1}^{N} p_i \text{ and } <T> = \frac{1}{N}\sum_{i=1}^{N} T_i \text{ (available routine in most spreadsheet programs)}$$

9.2.1. Error propagation

The 'error' ΔV in V (see Eq.9.2), depends on the errors in V_{stop} and V_{start} and the standard deviations of <T> and <p> ,$\sigma_{<T>}$ and $\sigma_{<P>}$.

The best estimate of the standard deviation σ of an averaged value is the square root of the variance. Therefore:

$$\sigma_{<p>} = \sqrt{\sigma_{<p>}^{\ 2}} = \sqrt{\frac{N}{N-1} < (\Delta p)^2 >} = \sqrt{\frac{N}{N-1}(< p^2 > - < p >^2)} \text{ (available in most spreadsheet programs)}$$

, and

$$\sigma_{<T>} = \sqrt{\sigma_{<T>}^{\ 2}} = \sqrt{\frac{N}{N-1} < (\Delta T)^2 >} = \sqrt{\frac{N}{N-1}(< T^2 > - < T >^2)} \text{ (available in most spreadsheet programs)}$$

Although measuring accuracy depends on the type of equipment, the following values are typical:

ΔV_{start}	≤ 2.10^{-4} [m^3]
ΔV_{stop}	≤ 2.10^{-4} [m^3]
σT	≤ 5 K [°C]
σp	≤ 1000 [Pa]

For calculation of the error ΔV in V, the general error propagation law (See Eq. 9.1) is applied:

$$\Delta V = \sqrt{\frac{<p>^2}{<T>^2}\frac{T_0^{\ 2}}{P_0^{\ 2}}\left(\Delta V_{stop}^{\ \ 2} + \Delta V_{start}^{\ \ 2} + \frac{\left(V_{stop} - V_{start}\right)^2}{<p>^2}\sigma_{<p>}^{\ \ 2} + \frac{\left(V_{start} - V_{stop}\right)^2}{<T>^2}\sigma_{<T>}^{\ \ 2}\right)} \text{(Eq. 9-3)}$$

Example 1 (sampled gas volume):

Suppose that <p> = 121300±1000 Pa <T>=297.2±5 K, V_{start} = 213.1230 ± 0.0005 m_n^3 and V_{stop} = 213.1780 ± 0.0005 m_n^3, then according to Eq. 9.2 V becomes (213.1780-213.1230)*(121300/101300)*(273.15/297.2) = 0.0061 m_n^3. The error in V is calculated by Eq. 9-3:

$$\Delta V = \sqrt{\frac{121300^2}{297.2^2}\frac{273.15^2}{101300^2}\left(0.0005^2 + 0.0005^2 + \frac{(213.1780-213.1230)^2}{121300^2}1000^2 + \frac{(213.1230-213.1780)^2}{297.2^2}5^2\right)} = 0.001$$

The sampled volume should be presented as V=0.061 ± 0.001 m_n^3. The relative error is 2.1%.

9.3. Gravimetric analysis

9.3.1. Determination of gravimetric tar content

It is assumed that enough solvent is used during extraction of the filter and rinsing of the impingers.

After distillation/evaporation of the bulk tar sample by rotary evaporation, the gravimetric mass of tar, M_T, is calculated by mass-subtraction of the tar containing 'constant' weight flask and the empty acclimatised flask:

$$M_T = M_{T1} - M_{T0} \text{ [kg]} \qquad \text{(Eq. 9-4)}$$

With:	$M_{T0} \pm \Delta M_{T0}$	Mass of the empty flask.[kg]
	$M_{T1} \pm \Delta M_{T1}$	Mass of tar containing flask after rotary evaporation. [kg]

When M_T is known, the concentration of gravimetric tar in producer gas can be calculated according to:

$$c_T = \frac{M_T}{V} \text{ [g/ m}_n^3\text{]} \pm \Delta c_T \qquad \text{(Eq. 9-5)}$$

9.3.2. Determination of particle content

The amount of particles is calculated from the difference in mass between the dry clean filter and the dry particle containing filter, obtained after sampling, storage in a solvent, extraction in a Soxhlet extractor and drying:

$$c_p = \frac{M_p}{V} = \frac{(M_{p1} - M_{p0})}{V} \text{ [kg/ m}_n^3\text{]} \pm \sigma c_P \qquad \text{(Eq. 9-6)}$$

With:	$M_{P0} \pm \Delta M_{P0}$	Mass of the dry clean filter (mg)
	$M_{P1} \pm \Delta M_{P1}$	Mass of the dry filter after usage and extraction (mg)

9.3.3. Error propagation

Application of the general error propagation law on Eq. 9-5 results:

$$\Delta c_T = \sqrt{\left(\frac{1}{V}\right)^2 \left(\Delta M_T^{\;2}\right) + \left[\frac{\left(M_{T1} - M_{T0}\right)}{V^2}\right]^2 \Delta V^2} \qquad \text{(Eq. 9-7)}$$

The error in M_T is:

$$\Delta M_T = \sqrt{\left(\Delta M_{T1}^{\;2} + \Delta M_{T0}^{\;2}\right)} \qquad \text{(Eq. 9-8)}$$

$\Delta M_{T,1}$ and $\Delta M_{T,0}$ represent the inaccuracy introduced by weighing of the flask. Reproducibility tests of the acclimatising method prescribed in section 8.1.4, show a weighing error of 2 mg the weighing of a flask, which is more than the analytical balance accuracy of 0.1 mg. However, R&D research by BTG and ECN has also shown that the maximum error ΔM_T is about 5 % of M_T for tar concentrations in isopropanol of about 1 g/l. Note that this error is not simply introduced by the limited precision of the weighing balance but also by other inaccuracies due to extraction, rotary evaporation and hydrogen bonding of the solvent.

Summarised:

D$\mathbf{M_T}$	$\sqrt{((2\cdot10^{-6})^2 + (2\cdot10^{-6})^2)} \leq \mathrm{D}\mathbf{M_T} \leq 0.05 \cdot M_T$ [kg]
D**V**	See section 9.2.

Similar to equation 9-7 the error introduced in the particle concentration is calculated by:

$$\Delta c_p = \sqrt{\left(\frac{1}{V}\right)^2 \left(\Delta M_p^{\;2}\right) + \left[\frac{\left(M_{p1} - M_{p0}\right)}{V^2}\right]^2 \Delta V^2} \qquad \text{(Eq. 9-9)}$$

According to section 7.1.2 particle sampling error is influenced by the deviation from isokinetic conditions, which in practice are never exactly reached and also depend on the gas flow in the duct. In case the sampling is conducted under the conditions of Eq. 7-2 the typical relative error in Mp will be about 5%.

Summarised:

D$\mathbf{M_p}$	$0.14\cdot10^{-6} \leq \mathrm{D}\mathbf{M_p} \leq 0.05 \cdot M_p$ [kg]
D**V**	See section 9.2.

Parallel measurements will provide more information on accuracy with respect to isokinetics and mass loss during post-sampling.

Example 2 (gravimetric tar):

If $M_{T1} = 126.3821 \cdot 10^{-3} \pm 2 \cdot 10^{-6}$ kg, and $M_{T0}=126.1705 \cdot 10^{-3} \pm 2 \cdot 10^{-6}$ kg, and $V=0.061 \pm 0.001$ m_n^3 (as in example 1), then according to Eq. 9.5 c_T is equal to $((126.3821 \cdot 10^{-3}-126.1705 \cdot 10^{-3})/0.061) = 3.496 \cdot 10^{-3}$ kg/m_n^3. Using an error of 5% in M_T, the error in c_T is calculated by Eq. 9-7as follows:

$$\Delta c_T = \sqrt{\left(\frac{1}{0.061}\right)^2 \left((0.05 \cdot 0.2116 \cdot 10^{-3})^2\right) + \left[\frac{\left(0.2116 \cdot 10^{-3}\right)}{0.061^2}\right]^2 0.001^2} = 0.1893 \cdot 10^{-3} \quad [\text{kg/ } m_n^3]$$

In this example the concentration of gravimetric tar in the gas phase is $c_P=3.5 \pm 0.2$ g/m_n^3 and the relative error is 5.4 %.

Example 3 (particle content):

Suppose that $Mp_1 =5.1631 \cdot 10^{-3} \pm 0.1 \cdot 10^{-6}$ kg, and $Mp_0=5.0020 \cdot 10^{-3} \pm 0.1$kg and $V=0.061 \pm 0.001$ m_n^3 (as in example 1), then according to Eq. 9.8 C_P is equal to $(5.1631 \cdot 10^{-3}-5.0020 \cdot 10^{-3})/0.061=2.6615 \cdot 10^{-3}$ kg/m_n^3. Using an error of 3% in M_p, the error in C_P is calculated by Eq. 9-8:

$$\Delta C_P = \sqrt{\left(\frac{1}{0.061}\right)^2 \left((0.03 \cdot 0.1611 \cdot 10^{-3})^2\right) + \left[\frac{(0.1611 \cdot 10^{-3})}{0.061^2}\right]^2 0.001^2} = 0.09719 \cdot 10^{-3} \quad [\text{kg/ } m_n^3]$$

In this example the concentration of gravimetric tar in the gas phase is $C_P=2.7 \pm 0.1$ g/m_n^3 and the relative error is 3.6 %.

9.4. Gas chromatographic analysis

9.4.1. Determination of individual compound concentrations

Individual tar compounds are identified by the mass selective detector (MSD) of the gas chromatograph (GC) and the use of model compounds. The gas content of tar components is calculated as follows (see also section 8.2.6):

$$c_A = \frac{M_A \cdot c_T}{M_S} = \frac{A_S \cdot M_{is} \cdot c_T}{A_{is} \cdot RF \cdot M_S} \pm \Delta C_A \, [\text{g}/m_n^3] \quad \text{(Eq. 9-10)}$$

With:

$c_A \pm \Delta c_A$	Concentration of compound A in the gas phase [g/ m_n^3]
$M_A \pm \Delta M_A$	Mass of component [kg],
$M_S \pm \Delta M_S$	Solved mass of gravimetric tar (usual 0.1 g)
$M_{is} \pm \Delta Mis$	Mass of internal standard [kg]
$A_s \pm \Delta A_s$	Area of compound
$A_{is} \pm \Delta A_{is}$	Area of internal standard
$c_T \pm \Delta c_T$	Gravimetric tar concentration [g/ m_n^3]
$V \pm \Delta V$	Sampled gas volume (m_n^3)

9.4.2. Error propagation

The error made in the determination of component concentrations can calculated by following formula, based on the general error propagation law.

$$\Delta c_A = \sqrt{\left(\frac{M_{iS} \cdot c_T}{A_{is} \cdot RF \cdot M_S}\right)^2 \Delta A_S^{\ 2} + \left(\frac{A_S \cdot c_T}{A_{is} \cdot RF \cdot M_S}\right)^2 \Delta M_{is}^{\ 2} + \left(\frac{A_S \cdot M_{is}}{A_{is} \cdot RF \cdot M_S}\right)^2 \Delta c_T^{\ 2}}$$

$$\sqrt{\ldots\ldots\ldots \left(\frac{A_S \cdot M_{iS} \cdot c_T}{A_{is}^{\ 2} \cdot RF \cdot M_S}\right)^2 \Delta A_{iS}^{\ 2} + \left(\frac{A_S \cdot M_{is} \cdot c_T}{A_{is} \cdot RF^2 \cdot M_S}\right)^2 \Delta RF^2 + \left(\frac{A_S \cdot M_{is} \cdot c_T}{A_{is} \cdot RF \cdot M_S^{\ 2}}\right)^2 \Delta M_S^{\ 2}} \qquad \text{(Eq. 9-11)}$$

10. Reports and documentation

10.1. 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, accuracy, percent RSD, matrix spike recovery 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.

10.2. 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 paragraph 10.4. The raw log data can be customised to suit a particular report or usage.

Four different numbers are reported in the Guideline, which are:

1. The concentration of gravimetric tar in g/m_n^3 (see Paragraph 8.1);
2. The concentration of the individual tar compounds as measured by GC (in a list as given in Appendix 13.2, compounds ranging from benzene to coronene, see Paragraph 8.2);
3. The sum of concentrations of GC-detected, identified compounds (sum of compounds reported in 2.);
4. The sum of concentrations of GC-detected, non-identified compounds in the range of benzene to coronene, 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 identified compounds might be that 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.

Remarks using suitable designations (see Appendix 13.7) should be provided with reported data to alert the user to some specific condition that may have affected the data.

Essential information to be contained in a report may be the following:

- The name of the laboratory (or factory), where the sample was received from
- 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 place, 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
- Analytical technique and parameter settings
- Target analytes values, usually reported in mg/m_n^3 or g/m_n^3
- Analytical precision and accuracy

10.3. Designation

Examples of designations (EPA, 1997) for an analysis data sheet are:

- “U” – The analyte was analysed for but not detected. The value preceding the “U” is the “minimum quantitation limit (MQL)”. Minimum Quantitation Limit (MQL) – Every sample has a concentration level below which the variance of the results for a particular analyte exceeds the acceptable quality control criteria. This level is the MQL and is based on the value preceding the “U”. The MQL is based on the lowest quantitative data point of the instrument calibration curve. The MQL is derived using this data point and other factors such as: sample size, dilution required, and sample interference. Analytes varies from analyte to analyte within a sample. Analytes are often detected at levels below the MQL and are reported as estimated values (J). Generally, analytes identified below the MQL will only be reported if the concentration is greater than one tenth of the MQL.

- “J” – The identification of the analyte is acceptable, but the quantitative value is an estimate. The value preceding the “J ” is the “estimated value”.
- “N” – There is presumptive evidence that the analyte is present but it has not been confirmed. The analyte is “tentatively identified”. Tentative Identification: There is an indication that the analyte reported is present. The quality control requirements necessary for confirmation were not met.
- “C” – The analyte is determined to be present. The presence of the analyte was “confirmed by GC / MS”.
- “A” – The analyte was analysed in replicate. The value preceding the “A” is an “average value” of the replicates.
- “K” – The analyte is determined to be present. The actual value is known to be “less than” the value preceding the “K”. Less Than Values – The analyte is present, but the amount of the analyte is determined to be below an acceptable level for quantitation. The concentration can not be calculated, but is determined to be less than the value given.
- “L” – The analyte is determined to be present. The actual value is known to be “greater than” the value preceding the “L”. Greater Than Values – The analyte is present, but the amount of the analyte is determined to be above an acceptable level for quantitation.
- “R” – Data is “rejected” and should not be used. Rejected data – some or all of the quality control data for the analyte were outside criteria. The presence or absence of the analyte can not be determined from the data. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

10.4. 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 13.7.

11. Safety aspects

This section is intended to briefly list potential dangers associated with tar analysis and recommended precautions to avoid exposure to hazardous chemicals and accidents. For a more comprehensive description of chemical safety issues, the reader should consult the reference sources at the end of the section.

11.1. 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.

11.2. 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.

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 reversible or irreversible and response time may be immediate or delayed several days depending on the rates of absorption, biotransformation, 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 nonpolar organic solvent vapours since they are the most volatile chemicals. In contrast to water-soluble chemicals and large molecules nonpolar solvents diffuse readily through the blood-brain barrier. About 90% of all occupational poisoning are caused by inhalation of nonpolar 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 Guideline, 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 (see Appendix 13.2) depending on the condition for 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. Phenol is considered as a co-carcinogen by many experts.

In view of the low volatility and pungent odour of many compounds excessive exposure to vapours does not seem likely unless fumes are generated by heating or leakage from gasifier or sampling system. 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 1000 Pa in a rotary evaporator. Similarly samples are often dried under vacuum in a desiccator.

When working with such devices 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 highly 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.

11.3. Safety precautions

One key to prevent accidents is to use the safest possible practices in laboratory. All chemical work should therefore be performed only by individuals with proper training and experience to deal with the expected risks and hazards during laboratory operations.

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[2], 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 laboratory work is being conducted:

- 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 sideshields, goggles, faceshield), protective gloves[3] and 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

11.4. 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 15-30 min 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 disposed of residues according to safe disposal procedures.

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

11.5. 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/ipcssyn.html

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

[3]: 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.

- 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/ngispgm3/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

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

12. References

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VDI 2066, part 1: *Measurement of particulate matter – Measurement of particulate matter in flowing gases. Gravimetric determination of dust load. Fundamentals*, VDI, October 1975

VDI 2066, part 2: *Measurement of particulate matter – Manual dust measurement in flowing gases. Gravimetric determination of dust load. Tubular filter devices (4* m^3/h*, 12* m^3/h, VDI, August 1993

VDI 2066, part 7: *Measurement of particulate matter – Manual dust measurement in flowing gases. Gravimetric determination of dust load. Plane filter devices*, VDI, August 1993

13. Appendices

13.1. 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 13-1) based on 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.

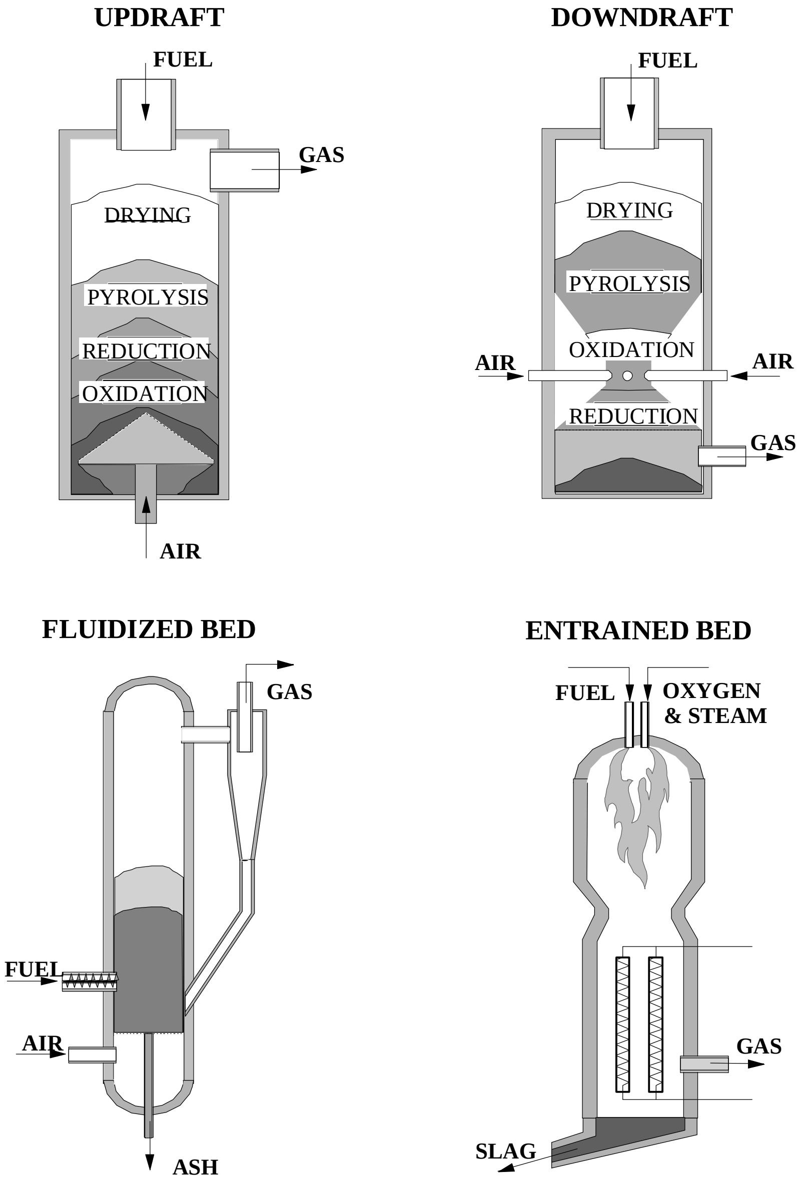

Figure 13-1: Schematic drawing of four basic gasifier types

In updraft gasifiers, the fuel generally moves from 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. 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 <2 cm. 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 13-1, 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^3_n	0.1 – 0.5	0.1 – 1	20 - 60
Tar (generic definition)	g/m^3_n	50 – 150	0.5 – 2	7 – 10

Table 13-1: Typical operating conditions and gas compositions of various wood fuelled gasifiers at atmospheric pressure. Data source (tar and particles): Milne et al 1998

13.2. Available list of organic condensable (“tar”) compounds to be analysed

In this table, compounds that are commonly measured are printed in standard style. Compounds that can be expected but are analysed less frequently or occur in lower concentrations are printed in *italics*.

Downdraft / Fluidised bed gasification	Pyrolysis and Updraft gasification
Phenols Phenol *Cresols (o, m or p)* *Xylenols* *(Methyl)Naphthols* **Furans** *Benzofuran* *Methylbenzofurans* *Dimethylbenzofurans* *Dibenzofuran* **Aromatic compounds** Benzene Toluene Xylenes (o, m and p) *Ethynylbenzene* *Styrene* Indene (1H-Indene) Methylindene **PAHs** (* indicate EPA list of 16 PAHs) Naphthalene* (1- or 2-) Methylnaphthalene Diphenyl Acenaphthylene* Acenaphtene* Fluorene* (9H-Fluorene) Phenanthrene* Anthracene* Fluoranthene* Pyrene* Benzo(a,b,c) fluorene *Benzo(a)anthracene** Chrysene* *Benzo(b***, j or k***)fluoranthene* *Benzo(a** *or e)pyrene* *Dibenzo(a,h)anthracene** *Perylene* *Indeno(1,2,3-cd)pyrene** *Benzo(g,h,i)perylene** *Dibenzopyrenes* *Anthanthrene* *Coronene* **Nitrogen containing aromatics** Pyridine Methylpyridines, Picolines (Iso)Quinonoline	**Acids** Formic acid, Propionic acid, Butyric acid Acetic acid **Sugars** Levoglucosan *Alpha-D-Glucose, Beta-D-Fructose, Cellobiosan* **Alcohols and phenols** *Methanol, Ethanol* Phenols, Cresols (o, m or p), Xylenols **Aldehydes and ketones** *Formaldehyde, Acetaldehyde* *Acetone* *2-Cyclopenten-1-one, (Methyl)- 2-Cyclopenten-1-one* **Guaiacols** Guaiacol, Creosol (= 4-methyl-guaiacol) Ethylguaiacol, Eugenol, Isoeugenol **Furans** Dimethylfuran, Furfural (2-furaldehyde) Methyl Furfural, Furfuryl alcohol *(Methyl- or dimethyl-)benzofurans and dibenzofurans* **Mixed oxygenates** Hydroxyacetaldehyde, Acetol, Vanillin Propanal-2-one, Glyoxal *2-hydroxy-3-methyl-2-cyclopentene-1-one* *(di-, tri-)Methoxybenzenes, Trimethoxyphenols* **Aromatic compounds** Benzene, Toluene, Xylenes (o, m and p) Ethynylbenzene Styrene Indene (1H-Indene), Methylindene **PAHs** (* indicate EPA list of 16 PAHs) Naphthalene* (1- or 2-) Methylnaphthalene *Diphenyl* Acenaphthylene* *Acenaphtene** Fluorene* (9H-Fluorene) *Phenanthrene**, *Anthracene**, *Fluoranthene**, *Pyrene** **Nitrogen containing aromatics** (Methyl)pyridines, Picolines, *(Iso)Quinoline*

13.3. List of individual organic compounds found in biomass producer 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	Sub1
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

13.4. Liquid Quench

The working principle of liquid quench with circulating fluid is shown in Figure 13-2. Liquid injection into the sample gas stream must occur immediately after the particle filter outlet. A liquid flow rate in the order 10 - 50 ml/min (depending on the sample gas flow rate) is sufficient to cool the gas from 250 to 50°C.

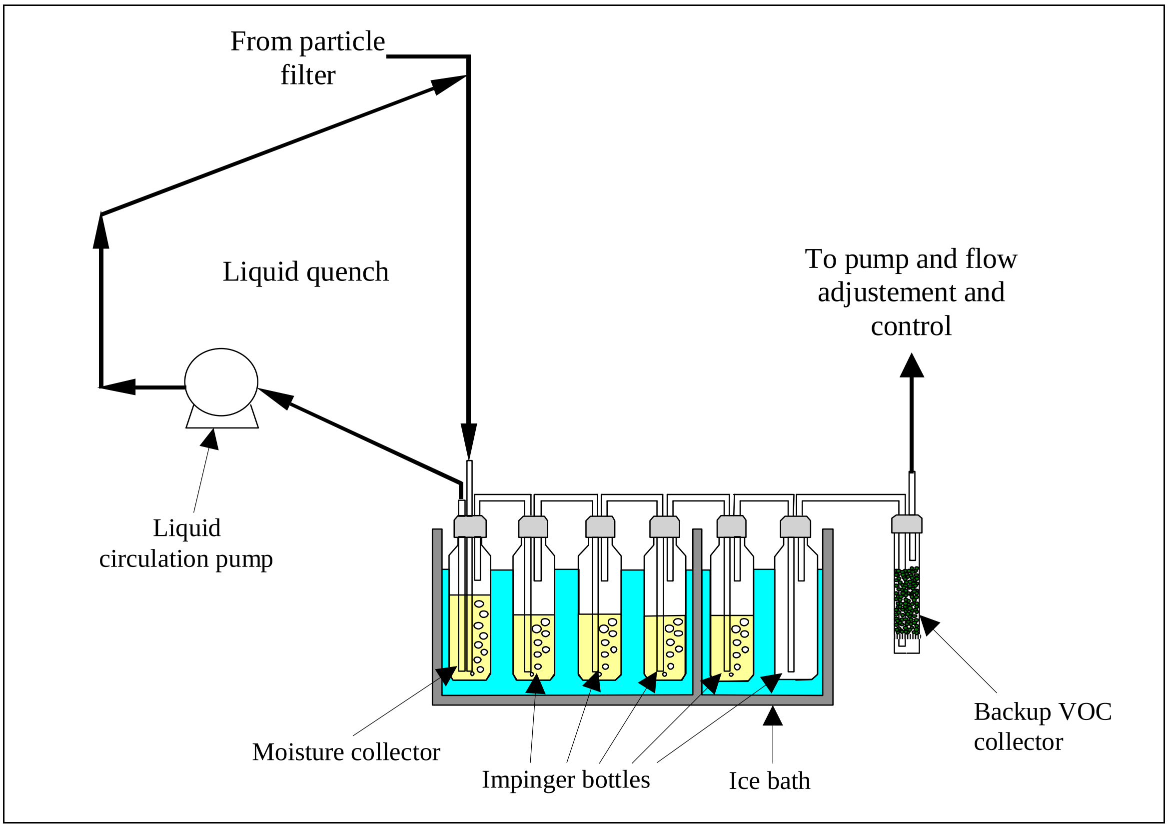

Figure 13-2: Liquid quench system as part of the sampling train arrangement

13.5. Modified (VTT) design of impinger bottles

The mass and heat transfer in impinger bottles can be improved by improving the design of impinger bottles. An improved design by VTT is shown in Figure 13-3. Glass bends using ball ground joints (Figure 13-3) 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.

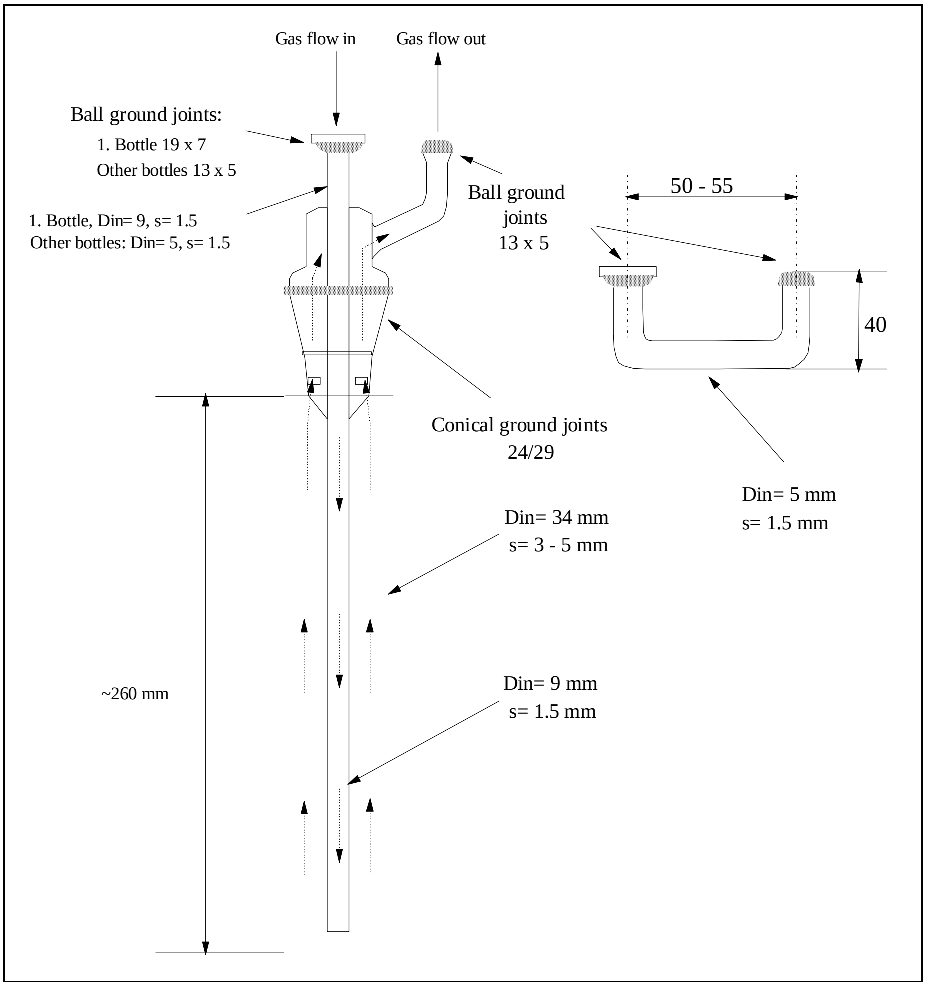

Figure 13-3: The impinger bottle and the glass bend used by VTT.

13.6. Alternative sampling train: the Petersen column

During preparation of the Guideline, the partners have gathered experience of the use of the described sampling train. The Danish participant, Danish Technological Institute (DTI), suggests that an alternative for module 3 proves more convenient when used in the field, compared to the standard configuration. It is DTI’s opinion that the use of a liquid quench and 6 washing bottles containing solvent in a cooling bath which also contains solvent means that the sampling staff to a great extent has to handle the solvent and is exposed to the solvent. Furthermore, there is a risk of aerosol penetration through module 3. Therefore, DTI developed an alternative sampling train, which possibly eliminates the disadvantages of module 3.

The new sampling train is called the ”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 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.

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.

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.

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 after the column and 85% of this penetration causes benzene. Furthermore, the "Petersen column" is easy to handle and the staff is hardly exposed to solvent steam from the washing and cooling medium. Figure 13-4 shows the "Petersen column".

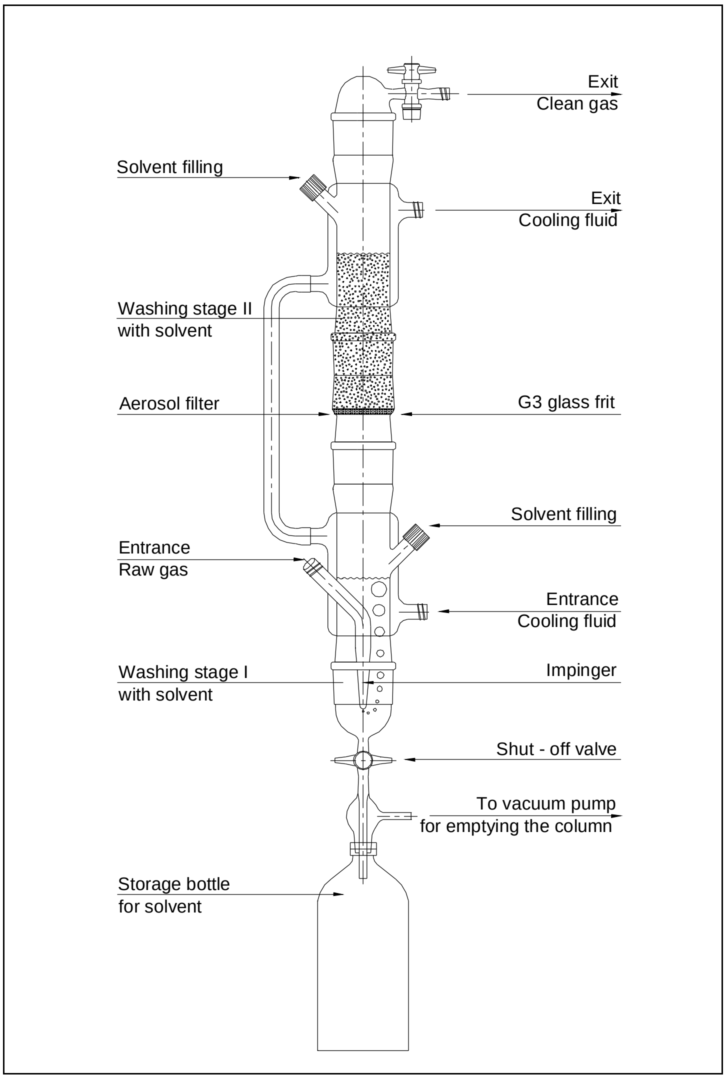

Figure 13-4 The "Petersen column"

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

13.7.1. 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):			[Nm^3/h] (if calc., spec. gas rate:		2,6	Nm^3/kg **wet**
Gasifier start *:				stationary since *:		
Fuel type *:		Pine wood chips (approx. 20 x 20 x 10 mm; 5 wt% sawdust), dried				
Fuel moisture *:			[%, dry basis]			
Actual fuel feeding rate *:			[kg wet/h]			
Sampling parameters						
Sampling site (hot/cold end):		Raw gas after gasifier				
Tar trapping solvent:		Isopropanol				
Ambient temperature:			[°C]			
Ambient pressure:		1000	[mbar]			
Duct diameter:			cm			
Diameter of sampling nozzle:			mm			
Particle filter temperature:		250	[°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:		n.d.	[g]			
Solvent from Soxhlet extraction:			[g]			
Total particle mass in filter tubes:			[mg]			
Normalised sampled gas flow rate:			[Nm^3/h]			
Remarks:		-Values given by the gasifier operators are marked with *.				
		- In the condenser, only Isopropanol is used.				
		- All the liquid is stored in one bottle (under nitrogen blanket and in a refrigerator).				

13.7.2. Parameter log for gas meter reading

Sampling of P&T from Biomass Producer Gases						
Gasifier Type/Site:		X				
Sampling site (hot/cold end):		Raw gas after gasifier			Date:	X
Test No.:		X				
Rated sampling gas flow rate (dry):			Nm^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]	[Nm^3/h]

Remarks:	- Condensation train: liquid quench, 1 condenser (0°C; Isopropanol), no saturator.					
	- Tar absorption train: 3 wash bowls with Isopropanol (type Dreschel, -24°C), drop separator					
	- Before the pump an activated carbon filter is used as pump, protection (lignite coke; Dreschel impinger)					
	- After a few minutes, aerosol formation occurs (as mist) in the sampling train.					
	Mist colour is white. Some mist is found before the coke adsorber.					
Averaged sample flow rate:			Nm^3/h			
Total amount of gas sampled:			Nm^3			
Total sampling duration:			hours			
Mean gas meter temperature:			°C			

13.7.3. Log for particulate measurement

Sampling of P&T from Biomass Producer Gases						
Gasifier Type/Site:		X			Date:	X
Sampling site (hot/cold end):		Raw gas after gasifier			Test No.:	X
Particle filter pre-treatment						
Type of particle filter used:		Munktell			Filter tube no.:	0
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:	The Soxhlet extraction is made immediately after the sampling.					
	The Soxhlet extraction is made with fresh solvent at ambient pressure.					
	No acetone rinsing is made.					
	The solvent in the Soxhlet thimble housing is colourless after hours of extraction.					
Particle filter post-treatment						
Post-conditioning temperature:				°C		
Post-conditioning duration:				hours		
Final tube weight after post-conditioning:				g		
Remarks:						

13.7.4. 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
