Investigating hot gas cleaning of woody biomass derived bio-syngas for SOFC operation

Master Thesis

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M Sustainable Energy Technology
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Abstract

In the current transition to new and durable methods of generating energy, biomass is becoming a primary source of energy. Solid Oxide Fuel Cells, when integrated in a combined heat and power system, can yield high efficiencies in the conversion from biomass to thermal and electrical energy. One of the challenges that this process faces is the damaging effects of the contaminants that are formed in the gasification of biomass fuels. These damage effects include the clogging up of lines, de-activation of the catalysts and a decreased carbon conversion. Among these contaminants, tars, particulate matter, HCl and H_2S are the most prominent and can cause severe damage on downstream equipment, interfere with electrochemical reactions and pressure drops, which all negatively affect the SOFC performance.

This study focuses on the effectiveness of a re-designed high-temperature gas cleaning unit on removing these contaminants. Under the FlexiFuel-SOFC project, which aims to develop a highly efficient fuel flexible biomass CHP system, an integrated system consisting of a gasifier, gas cleaning unit and a SOFC has been built in the laboratories of BIOS Bioenergiesysteme. HCl, H_2S and tar contents in the syngas were analyzed at different points in the process.

The operating temperatures are monitored to see if the design parameters are achieved. It is critical for each reactor/component to reach the design temperature, as this can greatly influence the gasification process, the effectiveness of catalysts and fuel cell bio-syngas to electrical energy conversion.

The temperature evaluation shows a normal heating up of the gasifier and reactors during the test runs. The design temperature parameters were achieved.

The tar content analysis shows the most abundant tar compounds were naphthalene, toluene and phenol. The total tar content in the syngas was measured on two test days and was found to be 3.64 and 3.37 g/nM^3 before gas cleaning and 0.11 and 0.41 g/Nm^3 after gas cleaning, which comes down to a 97% and 88% resp. reduction in total tar content.

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Nomenclature

Abbreviation	Description	Abbreviation	Description
AFC	Alkaline Fuel Cell	**LHV**	Lower Heating Value
ATM	Atmospheric	**MCFC**	Molten Carbonate Fuel Cell
BFBG	Bubbling Fluidized Bed Gasifier	**MW**	Molecular Weight
CFBG	Circular Fluidized Bed Gasifier	**N**	Normal
CHP	Combined Heat and Power	**NDIS**	Non-Dispersive Infrared Spectroscopy
DFAFC	Direct Formic Acid Fuel Cell	**NPSH**	Net Positive Suction Head
DFBG	Dual Fluidized Bed Gasifier	**P**	Pressure
DFFC	Direct Formate Fuel Cell	**P&ID**	Piping and Instrumentation Diagram
DMFC	Direct Methanol Fuel Cell	**PAFC**	Phosphoric Acid Fuel Cell
EFG	Entrained Flow Gasifier	**PAH**	Polycyclic Aromatic Hydrocarbon
ER	Equivalence Ratio	**PEMFC**	Proton Exchange Membrane Fuel Cell
ESP	Electrostatic Precipitation	**PG**	Plasma Gasifier
FT	Fischer Tropsch	**ppm**	Parts per million
FTIR	Fourier-Transform Infrared Spectroscopy	**RDF**	Refuse Derived Fuel
GC	Gas Chromatograph	**SOFC**	Solid Oxide Fuel Cell
GCMS	Gas Chromatograph Mass Spectroscopy	**T**	Temperature
GCU	Gas Cleaning Unit	**UFB**	Updraft Fixed Bed
H	Enthalpy	**UV-VIS**	Ultraviolet-Visible Spectroscopy
ICE	Internal Combustion Engine	**Vol.**	Volume
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy	**YSZ**	Yttrium Stabilized Zirconia

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1. Introduction

Oil, gas and coal reserves are expected to be depleted in the next 50, 52 and 134 years respectively. (BP, 2017) In the current transition to new and durable methods of generating energy, biomass is becoming a primary source of energy. Biomass materials can be turned into hydrogen and syngas which can provide heat and electricity which can be harvested and used for many types of applications. However, one of its disadvantages is that during the production of biomass derived syngas, poisonous contaminants are formed. The term 'contaminants' is used collectively to describe compounds that will degrade downstream applications such as fuel cells, engines and turbines, when present in certain concentrations. (Liu, 2014) These compounds include ammonia (NH_3), hydrogen cyanide (HCN), hydrogen sulfide (H_2S), hydrogen halides and halogens like hydrogen chlorine (HCl) and chlorine (Cl), trace metals such as sodium (Na) and potassium (K), particulate matter and tars. (Abdoulmoumine, 2015) (Aravind P. V., 2012)

Syngas produced from biomass gasification, so-called bio-syngas can be used as a fuel for Solid Oxide Fuel Cells (SOFCs) if the content of the trace species such as tars, chlorine and sulphur can be properly controlled. (Hofmann, 2009) The most prominent among the trace species is tar. It is known that, even though tar can possibly poison the fuel cell through carbon deposition, it may also become a fuel for SOFCs. (Liu, 2014) Under the SOFC conditions that are favourable for tar reforming, theoretically the SOFC could perform as a tar reformer in addition to the role being a generator for electricity production. Most of the experimental works published on this topic investigate the impact of simulated product gas on single SOFC performance while research with an integrated setup (gasifier - gas cleaning unit - fuel cell stack) with real bio-syngas remains limited. Currently, the impact of real tar on SOFC stack is yet to be understood and has limitedly been experimentally studied under SOFC stack conditions. Therefore, still extensive studies are required for developing SOFC stack at safe operation mode with high efficiencies. On top of the need of more studies using real tar containing bio-syngas, also the cross influence of tar and other compounds such as HCl and H_2S has to be investigated in more detail. (Cavalli A. et al., 2019)

This results in a small amount of tar species that enter the anode side and causes carbon deposition which in turn affects cell performance. (Lorente, 2012) Studies have researched the effect of temperature, current density and temperature on carbon deposition but not always with real syngas and with limited operation conditions. Several researchers suggest above 750 °C, small amounts of tar will not affect SOFC performance, while under 650 °C it may cause breaking of cells, clogging of the lines and overall a lower life cycle.

HCl and H_2S are also considered contaminants to the cleaning stage and the fuel cell, because they cause degradation of the catalyst material and de-activation of the anode material in a fuel cell. For example, in a SOFC with Ni/YSZ anode material, HCl has been found to react with Ni, which lead to performance losses and permanent surface structure changes. (Xu, 2010) Different anode and catalyts materials have been developed to lengthen their lifetime by increasing its resistance to HCl, H_2S and other contaminants.

In order to ensure safe operation of the stack and not damage the cells, there are contaminant limits to the inlet fuel that enters the stack's anode side. For the setup used here, these limits are: HCl < 5 ppmv, H2S < 1 ppmv, particulate matter < 0.1 mg/Nm^3 and tar < 1 ppm. This is then also the criteria for the GCU to clean the gas from the gasifier and it should be designed to reach at least these levels.

The syngas obtained from biomass gasification must first pass a Gas Cleaning Unit (GCU) to clean the gas from its main pollutants. TU Delft and HYgear have built a high-temperature GCU and installed and tested it at BIOS. Out of these test runs new insights were obtained and based on the feedback from the 1st generation model, the GCU is re-engineered into a 2nd generation GCU (GCU2). The aim of this thesis is to investigate the performance of this new GCU2 design.

The main research objective is to investigate the effectiveness of the GCU2. This will be done through:

- H_2S measurements
- HCl measurements
- Tar analysis
- Temperature evaluation of the integrated system

The structure of this report is as follows. First, the theory of how biomass is converted to electricity is given and the different types of gasifiers, gas cleaning units and fuel cells are described in Chapter 2. In Chapter 3 the methodology of the experiments is described. The results and discussion of the experiments are given and analyzed in Chapter 4, followed by the conclusion in Chapter 5.

2. Technology description and literature review

In order to generate electricity from biomass, three main stages are required (figure 1). (1) The process starts with the thermochemical conversion via gasification of solid biomass in order to produce syngas. This raw syngas contains the chemical energy required to drive the fuel cell. Before this syngas can be fed to the fuel cell, it must be cleaned from the contaminants and impurities. (2) This is done by leading the syngas produced from the gasifier to a gas cleaning unit (GCU). The purpose of the GCU is to clean the raw syngas so that it isn't harmful for the fuel cell to operate. The main contaminants the GCU filters are chlorine, sulphur, particulate matter and tars. (3) After running the raw syngas through the GCU, clean syngas is produced which is fed to the fuel cell. The fuel cell converts the chemical energy stored in the bonds of the molecules in the syngas into electrical energy which is the output product of this process. In this chapter each of these three stages is elaborated more on.

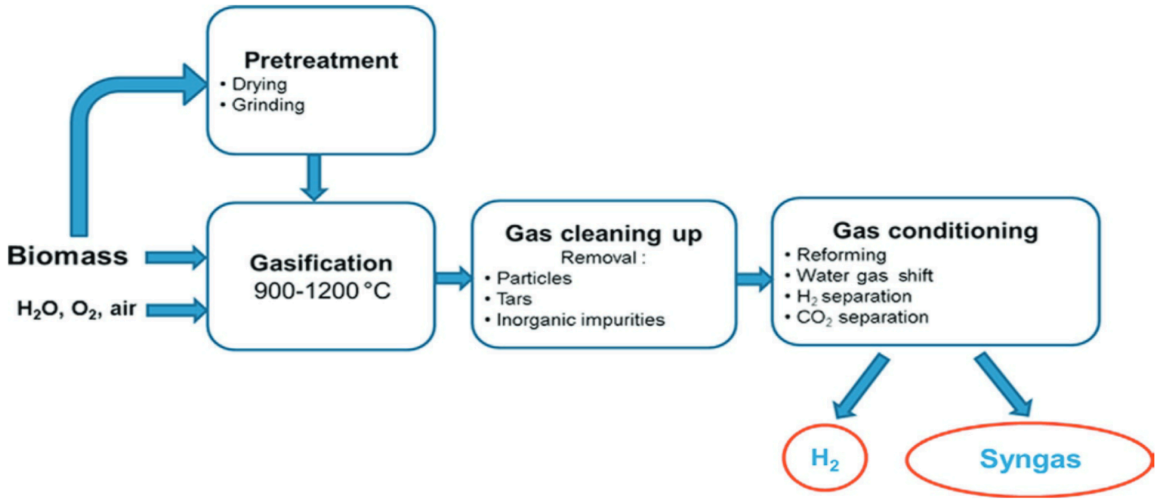


Figure 1 From biomass to syngas; a schematic overview of the multistage process. (Richardson, 2015)

2.1 Biomass to raw Syngas

Syngas is an intermediate gas that is needed to extract electrical energy from biomass. This synthetic gas can be formed from carbon-rich materials such as oil, coal or biomass. There are two main categories of processes through which syngas can be derived. The first category is through thermochemical processes, reforming (with steam), partial oxidation, pyrolysis or gasification. The other category contains biological processes such as photo-fermentation, dark-fermentation and (in)direct bio-photolysis. (Peres, 2013) The composition of the syngas differs greatly with different synthesis processes and materials, but usually consists mainly of CO and H_2 and also contains amounts of H_2O, CO_2, and

CH_4, N_2 and higher hydrocarbons. (U.S. Department of Energy National Energy Technology Laboratory., 2019)

Almost half of the syngas that is produced comes from coal, 25% comes from petroleum and 20% from naturel gas. Approx. 1% of from the syngas is derived through gasification of biomass. (U.S. Department of Energy National Energy Technology Laboratory., 2019)

There are several types of biomasses that can be used to convert to syngas. These biomass fuels include plants, wood, algae, manure etc. and each have different energy contents and properties. Biomass materials can be assigned to four main classes, which are: energy crops, agriculture crops, forestry waste and residues, and industrial and municipal wastes. (Meng Ni, 2006) (Kataki, 2015) Pandey et al. provide four generations of biomass: (Bhaskar, 2015)

- 1st generation: derived from edible materials
- 2nd generation: derived from nonedible materials such as forest residues
- 3rd generation: derived from aquatic biomass
- 4th generation: derived from engineered plants and microorganisms.

Gasification is a thermochemical process in which carbon-rich feedstock is converted in to a gas that usually contains hydrogen, carbon monoxide, nitrogen, and methane. The feedstock is fed into a gasifier, which is heated up to temperatures ranging from 600 °C to well over 1000 °C. Through partial oxidation of the biomass, in the presence of a gasification agent, a gas is formed. This raw syngas usually holds a lower heating because it still contains impurities and contaminants, which can cause issues on downstream equipment. In order to increase overall efficiency of the process, the syngas should be cleaned (Chapter 2.2). Pre-treatment of the biomass is required to meet the operation conditions of the gasifiers and it increases overall efficiency. Pre-treatment steps include separation, size reduction, palletization and drying. (Richardson, 2015)

In this project woody biomass is used as a fuel for the gasification step (2nd generation biomass).

2.1.1 Types of Gasifiers

Several designs of gasifiers reactors exist, each having their own (dis)advantages and purposes. Figure 2 shows the different design aspects of a gasifier.

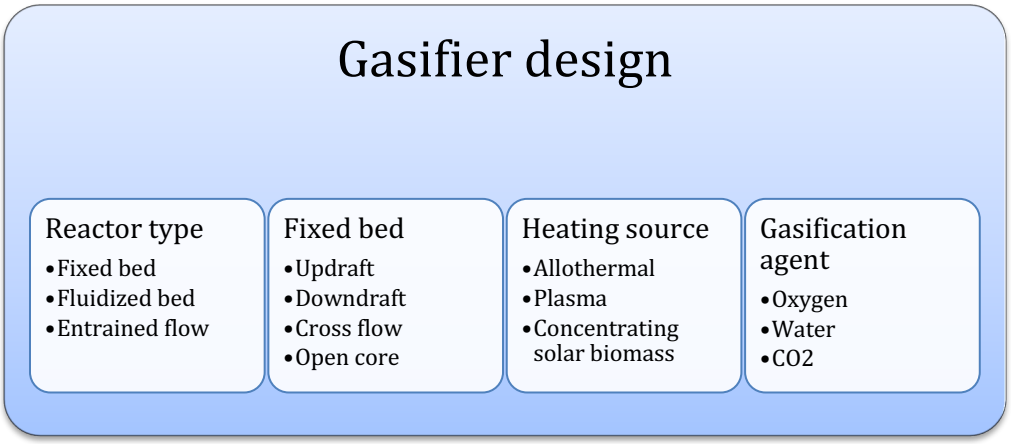


Figure 2 Classification of gasification processes.

The most commonly used gasifiers are described in the subsections below.

Updraft Fixed Bed Gasifier

In an Updraft Fixed Bed (UFB) gasifier (figure 3) biomass feedstock is fed to the gasifier chamber from the top or side. The produced gases are collected at the top and thus the feedstock and gas move in opposite directions. Gasification in these kind of gasifiers occur at temperatures of around 1000 °C. (Couto, 2013) (E4tech, 2009)

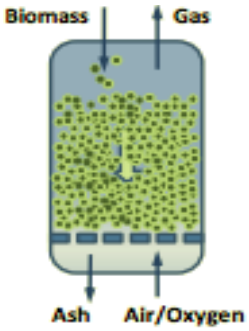


Figure 3 Updraft Fixed Bed Gasifier

Downdraft Fixed Bed Gasifier

In a Downdraft Fixed Bed (DFB) gasifier (figure 4) the biomass is fed from the top and the produced gases are extracted from the bottom. One advantage over an updraft gasifier is that a downdraft gasifier can achieve higher quality syngas. This is due to the fact that the gas has to go through a bed of glowing charcoal which reduces the tars. the main disadvantages are that this gasifier can only be operated with certain feedstocks, depending on size and density, and that generally it has low thermal efficiencies. (Couto, 2013)

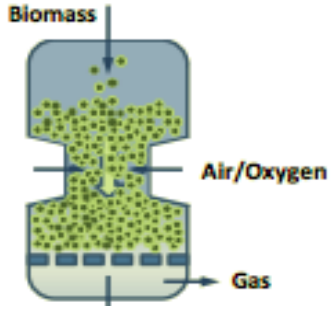


Figure 4 Downdraft Fixed Bed Gasifier

Entrained Flow Gasifier

An Entrained Flow (EF) gasifier (figure 5) uses powdered feedstock that comes in from the top and passes a high temperature flame at around 1200 to 1500 °C. The very high operation temperatures ensure a fast gasification of the feedstock and a higher quality of syngas. (Couto, 2013) However, since syngas outlet temperatures are very high, they generally need to be cooled down to be processed further (such as for gas cleaning), which decreases thermal efficiency of the system. (E4tech, 2009)

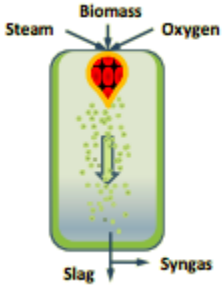


Figure 5 Entrained Flow Gasifier

Bubbling Fluidized Bed Gasifier

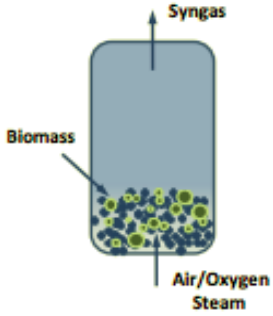


Figure 6 Bubbling Fluidized Bed Gasifier

In a Bubbling Fluidized Bed (BFD) gasifier (figure 6), gas (usually air or steam) is blown through the bed that consists of a bed material such as silica sand. By blowing the gas through the bed at a relatively low velocity (around 1 m/s), the bed acts as a fluid. Biomass feedstock is then mixed in the fluidized bed. By bubbling the bed, the biomass particles are in greater contact with the bed material and thus a better heat exchange takes place. (E4tech, 2009) A major disadvantage of this type of gasifier is that it can only be fed certain types of biomass that have low content of ash and alkali metals, since these can cause blockages in the lines. (Couto, 2013)

Circulating Fluidized Bed Gasifier

The Circulating Fluidized Bed (CFB) gasifier works similarly to the BFD gasifier described above. The main difference being the velocity of the gas that is blown through the solid bed material (Figure 7). Generally, gas velocities of 3 to 10 m/s are used. At these velocities gas and solid particles are blown upwards and they are separated in the cyclone, in which solid bed material is recycled to the fluidized bed and syngas is extracted. (Bingyan, 2009) The main advantage of a CFB gasifier over a BFD gasifier is that it enhances heat and mass transfer and increases the reaction rate. (Couto, 2013)

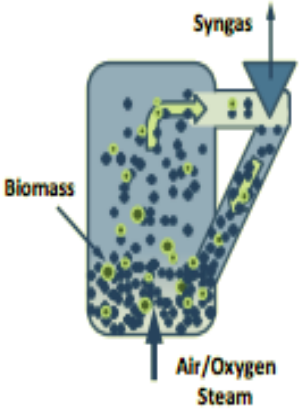


Figure 7 Circulating Fluidized Bed Gasifier

Dual Fluidized Bed Gasifier

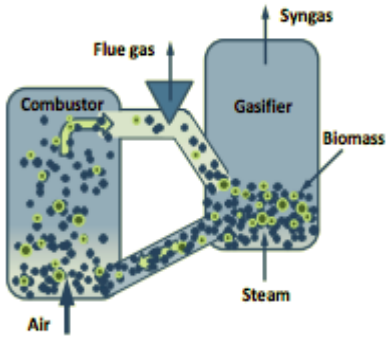


Figure 8 Dual Fluidized Bed Gasifier

A Dual Fluidized Bed (DFB) gasifier (figure 8) consists of two chambers, one in which gasification takes place, and another in which combustion takes place. Biomass is fed into the gasifier chamber and the resulting syngas and char is fed into the combustion chamber. The char is burnt in air and the bed material, which is carrying heat, heats up the gasifier chamber. This process allows to produce high caloric syngas, with low levels of nitrogen dilution. (Suda et al. 2007)

Plasma Gasifier

In a Plasma Gasifier (PG), biomass waste is superheated by running an electrical discharge through it, disintegrating the compounds to their atoms (figure 9). (Mountouris, 2006) Some of the main advantages of a PG is that it can produce the highest amount of energy per biomass, compared to other gasification process types, and that it can handle any type of (mixtures of) biomass. (Janajreh, 2013) However, achieving these superheated temperatures requires a high electricity input. (Global Syngas Technologies Council, 2019)

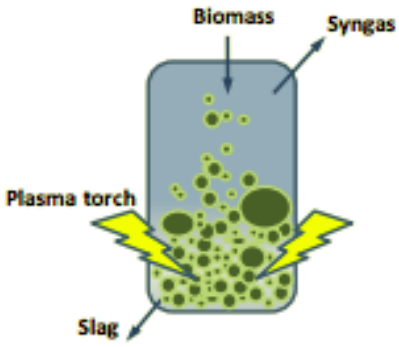


Figure 9 Plasma Gasifier

2.1.2. Chemical reactions during biomass gasification

Despite having different types of gasifiers with different working principles and operating conditions, there are four general processes that occur during gasification in all of the different types of gasifiers: 1) pyrolysis, 2) devolatilization, 3) partial oxidation, and 4) reduction. (Richardson, 2015)

During pyrolysis and devolatilization, the biomass material is heated up without oxygen as gasification agent. The feedstock is turned into gaseous, liquid and solid products (1). This step can be written down in the following chemical reaction: (Gómez-Barea, 2010)

$$\text{Biomass} \rightarrow \text{char} + \text{tars} + H_2O + \text{other gases} \qquad \Delta H^0 : 0 \ \text{kJ mol}^{-1} \quad (1)$$

The other gases that are formed include CO, CO_2, H_2, CH_4, N_2. Depending on the amount of oxygen that is available, the char can then either combust completely (producing CO_2) or partially (producing CO). The complete (2) and partial (3) combustion of char happens according to the following reactions:

$$C + ½\ O_2 \rightarrow CO \qquad \Delta H^0 : -111\ kJ\ mol^{-1}\ (2)$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H^0 : -394\ kJ\ mol^{-1}\ (3)$$

Carbon monoxide is released during the partial oxidation of char, which allows for char gasification. This process consists of three reactions that occur simultaneously: Boudouard reaction (4), steam gasification (5), and hydrogenic gasification or methanation (6).

$$C + CO_2 \rightleftarrows 2\ CO \qquad \Delta H^0 : +173\ kJ\ mol^{-1}\ (4)$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H^0 : +131\ kJ\ mol^{-1}\ (5)$$

$$C + H_2 \rightleftarrows CH_4 \qquad \Delta H^0 : -75\ kJ\ mol^{-1}\ (6)$$

After these reactions, all solid material is turned in to gas and liquids and in this mixture of gases the following homogeneous reactions occur:

$$CO + ½\ O_2 \rightarrow CO_2 \qquad \Delta H^0 : -283\ kJ\ mol^{-1}\ (7)$$

$$H_2 + ½\ O_2 \rightarrow H_2O \qquad \Delta H^0 : -242\ kJ\ mol^{-1}\ (8)$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \qquad \Delta H^0 : -283\ kJ\ mol^{-1}\ (9)$$

$$CO + H_2O \rightleftarrows CO_2 + H \qquad \Delta H^0 : -41\ kJ\ mol^{-1}\ (10)$$

$$CO + 3\ H_2 \rightleftarrows CH_4 + H_2O \qquad \Delta H^0 : -206\ kJ\ mol^{-1}\ (11)$$

The syngas that is formed through biomass gasification can be used for different purposes. In this research, the focus is on utilizing the syngas to generate power downstream through a SOFC system. Other syngas utilizations include the production of hydrogen, the synthesis of methanol and dimethyl ether (DME), the synthesis of Fischer-Tropsch fuels, or for a Combined Heat and Power (CHP) generation system.

- Hydrogen production and chemical reactions
- Methanol and DME synthesis and chemical reactions
- Fischer-Tropsch (FT) fuels and the chemical reactions

2.1.3 Influences on syngas composition

Converting biomass through means of thermal gasification is a process in which the overall efficiency depends on many factors. As mentioned in Chapter 2.1.1, the type of gasifier, as well as the type of gasifying agent (Chapter 2.1.2) play a major role in the conversion into syngas and can greatly affect the syngas composition, tar and char conversion, LHV and the cleaning of poisonous contaminants. The main factors that contribute to biomass gasification performance are: 1) gasifier temperature, 2) gasification agent, 3) biomass particle size, 4) gasifier type. These factors will be discussed in this chapter.

1) influence due to gasifier temperature

The effect of changing the gasifier temperature on the gasification process is a correlation that is easily to find and one that most researchers agree on. With higher temperatures in the gasifier, a higher conversion of carbon is obtained. The amount of char residue is also found to be lower with increased temperatures, which results in the quality of the syngas to be higher as it contains less tar volatiles and less effort on tar reforming is required downstream the gasifier. Higher gasifying temperatures also result in a higher rate of the endothermic reactions which, in particular the Boudouard reaction (4). (Couto, 2013)

2) influence due to gasification agent

Generally, air, pure O_2, steam, CO_2 or a mixture of these, is used as the gasifying agent in the process. The dynamics of the gasification process can vary greatly depending on the chosen gasifying agent. Operation costs, syngas composition, syngas heating value, heat production, and char and tar content all can increase or decrease depending on the chosen gasifying agent. (Wei, 2007)

Since air naturally contains a high percentage of N_2, the syngas that is formed with air as a gasifying agent will also contain a high fraction of N_2, which lowers the heating value of the syngas. (Situmorang, 2020) Depending on the equivalence ratio (ER), partial oxidation will occur when using air as a gasifying agent. This is the ratio of O_2 required for gasification to O_2 required for complete combustion and is an important factor for knowing the heating value of the product gas. (Wang L. W., 2008) A higher ER also reduces the amount of tar in the gasifier, since more O_2 is available to oxidize the volatiles of the tar compounds.

Looking at the stoichiometry of reaction (3), it is obvious that an ER of 2 provides for complete combustion. However, such high ER should be avoided as it generally results in lower CO and H_2 content and higher CO_2 content and thus lowers the heating value of the syngas. An ER of 0.2-0.4 is generally recommended to minimize the production of tar. (Situmorang, 2020)

Steam and CO_2 can also be used as gasifying agents in the biomass gasification process. Syngas formed in this way usually contains a higher H_2 concentration and has a higher heating value, but require more heat from external sources which can bring down thermal efficiency. (Wei, 2007) Another disadvantage of using steam or CO_2 as gasifying agents is that the syngas will contain more tar and thus catalytic reforming of these tars is required (more on in Chapter 2.2.4). It is found that with a decrease in temperature of the gasifying bed, a decrease in H_2 production occurs.

The different types of gasifying agents (air, steam, CO_2, O_2, or a mixture of these) and their advantages and disadvantages, collected from various research papers, can be found in the table below (table 1).

Table 1 Overview of the advantages and disadvantages of using different gasifying agents in biomass gasification.

Gasifying agent	Advantages	Disadvantages	Main references
Air	1. Allows partial combustion which supplies heat 2. Minimize tar content through ER 3. Higher gas yield	1. Lower LHV of syngas 2. More N_2 in syngas 3. Difficult to control ER	(Wang L. W., 2008) (Gil, 1999) (Situmorang, 2020)
Steam	1. Higher LHV of syngas 2. More H_2 in syngas 3. Higher power output and exergy efficiency in an integrated gasification-SOFC system 4. Less vulnerable to decrease in H_2 due to temperature decrease.	1. Endothermic reactions lower reactor temperature and external heat is required 2. Increased tar content in syngas 3. Requires catalytic tar reforming 4. Lower gas yield	(Wang L. W., 2008) (Alauddin, 2010) (Gil, 1999) (Shayan, 2019) (E. Shayan, 2018)
CO_2	1. Higher LHV of syngas 2. More H_2 and CO and less CO_2 in syngas	1. External heat is required 2. Requires catalytic tar reforming	(Wang L. W., 2008)

O_2	1. Medium LHV of syngas 2. High H_2 and CO concentration in syngas. Highest CO concentration compared to other gasifying agents.	1. Higher operating costs due to pure O_2 production	(Alauddin, 2010) (Situmorang, 2020)
Steam-O_2 mixture	1. Higher LHV of syngas 2. More H_2 and less N_2 in syngas (compared to air) 3. Heat is supplied through partial oxidation	1. Makes operating costs significantly higher due to use of pure O_2	(Alauddin, 2010) (Gil, 1999) (Situmorang, 2020)

3) influence due to biomass particle size

The size of the biomass particles has a strong influence on the gasification process and the syngas output. (Inayat, 2016) Bigger biomass particles are more difficult to burn since they have less surface temperature for the reactions to occur. Also, the geometry of a bigger size particle, compared to smaller size particles with the same total volume as the bigger particle, allows for less heat induction and in general its heat transfer to the core is less favorable. (Yahaya, 2019) On the other hand, small biomass particles will burn more easily and speed up the rate in which the gasification reactions occur. (Kumar, 2018)

Also, less char is formed when using small particle biomass compared to bigger particles. (Parthasarathy, 2014) It should be noted that to prepare small particle biomass, usually some kind of pre-treatment is required, such as chopping or pressurizing, which is energy consuming and therefore has a (slightly) negative impact on the total efficiency of the gasifier-SOFC system. (Situmorang, 2020) The findings on the effect of particle size in gasification on gas yield and LHV of some papers has been summarized below in table 2. (Couto, 2013)

Table 2 Gas yield and LHV of different biomass particle sizes. (Couto, 2013)

Range of particle size tested (mm)	Gas yield	LHV (MJ/Nm^3)	Reference
< 0.15, 0.15 - 1, 1 - 2, 2 - 5	2.16 - 2.41 m^3/kg	8.99 - 10.28	(Li J. Y., 2009)
0.2 - 0.3, 0.3 - 0.4, 0.45 - 0.6, 0.6 - 0.9	1.53 - 2.57 m^3/kg	7.0 - 8.7	(Lv, 2004)
< 0.3, 0.3 - 0.5, 0.5 - 1.0	72.74 - 74.79 wt%	11.8 - 15.26	(Mohammed, 2011)

It is found that for optimal gas yield, composition and LHV that biomass particle size should be as small as possible, with the most optimum results achieved with particle sizes in the range of < 0.3 mm and 0.3 – 0.5 mm.

4*) influence due to gasifier type*
As described in Chapter 2.1.1, different types of gasifier exist that can be used for biomass gasification. The types of gasifiers each have varying operating conditions and can handle different types of biomass feedstock, thus producing syngas with different properties. (Erakhrumen, 2012) The types of gasifiers differ from each other in the way the how the biomass is fed to the gasifier, the heat management design and how the feedstock and gasifier agent flow. (Ahmad, 2016) In a report from Alauddin et al., fixed and fluidized bed reactors are compared. Alauddin et al. argue that in a fixed bed reactor high amounts of char and tar is produced due to due to low and non-uniform mass and heat transfer between the biomass material and the gasification agent. On the other hand, fluidized bed reactors provide conditions in which conversion and reaction rates are improved due to a better contact between feedstock and gasification agent, as well as due to a better mixing. (Alauddin, 2010) In a recent study of Park et al., a downdraft fixed bed reactor and a bubbling fluidized reactor, using RDF (Refuse Derived Fuel) as fuel, were compared in terms of syngas composition, yield and quality. In this research, syngas derived with a bubbling fluidized reactor turned out to be of higher gas quality and LHV. (Park, 2018)

2.2 Cleaning the raw syngas

The main pollutants in the syngas are H_2S, tar, HCl and particulate matter. The levels of contaminant allowed downstream depends on the application of the syngas. For electricity production via SOFCs, the maximum levels of contamination allowed in this system are: HCl < 5 ppm, H_2S < 1 ppm and particulate matter < 0.1 mg/Nm^3. (FlexiFuel-SOFC, 2016)

There are different methods to clean each of the mentioned contaminants, of which the most conventional ones are described below.

2.2.1 Particulate matter removal

In coal or biomass gasification, generally ceramic candle filters are used to filter particulate matter from the gas. However, cleaning with this filter currently has three main challenges remaining: 1) its ability to clean gas to below specified limits of the system (i.e. turbine or fuel cell), 2) have a small pressure drop and 3) to maintain uptime during operation without the need for regular maintenance to clean the filter. The most important reasons for failure of the filter are filter unit and candle design, type of material used, thermal transient and ash deposition.

Thermal transient occurs when there is a rapid change in temperature, for example when the filter is cleaned by back blowing with cold gas. This rapid change in temperature may

have effect on the tensile strength and may cause deformation of the filter. The effect of thermal transient depends greatly on the thermal properties of the filter material used. For instance, metal filters have a greater thermal conductivity than aluminum oxide-based filters, and thus show less signs of deformation. An added benefit is that the fact that there is no or little deformation allows for a thinner wall for the filter which in turn help decrease pressure drop. However, the use of metal-based filters brings rise to other issues such as corrosion, cost and quality control. (Sharma, 2008)

Most turbine systems have a tolerance of particulate matter of 2 ppmw or lower. Aside from these design and material issues, there are some fundamental limits due to natural correlations. Increasing the porosity of the material increases the performance of the filter, but also increases filter surface area and the corrosion rate. Also, increasing the porosity of the material decreases mechanical strength as the porosity is inversely proportional to the mechanical strength. (Sharma, 2008)

2.2.2 HCl removal

Hydrogen halides such as HCl can be removed through different methods that are dependent on the temperature at which the gas is cleaned. Two temperature ranges can be defined: cold gas cleaning, which is usually done at or below room temperature and hot gas cleaning which is done at temperatures above 300 °C. The main advantages of cleaning at cold temperatures is because of a high removal efficiency and that it is a validated method widely tested and used in the research literature. The main disadvantage is that it requires the gas to be cooled down from 800-900 °C (from gasification) and this means that this incurs an extra loss on efficiency. (Abdoulmoumine, 2015) Removing HCl from a cold process is done by a method that relies on the solubility of HCl in water. The solubility of HCl is 82.3 g HCl/100g water at 0 °C and 67 g HCl/100g water at 30 °C. (U.S. National Library of Medicine National Center for Biotechnology Information, 2019) HCl is a strong acid that in an aqueous solution ionizes completely according to the following reaction.

$$HCl\ (g) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq) \qquad (12)$$

Caustic water (water with dissolved NaOh) can also be used as a solvent to remove HCl. In this solvent, HCl reacts with NaOH to form solid NaCl particles which can be easily precipitated out of solution. An added benefit of using caustic water over water is that it can also remove parts of H_2S and CO_2. (Allegue, 2012)

In hot operation HCl is removed through adsorption. The HCl-contaminated gas is passed through a reactor containing a sorbent that is capable of extracting HCl from the gas. Several types of sorbent are available for HCl removal. These sorbents mainly include

metals from two groups: alkaline earth and alkali metals. TU Delft performed sorbent testing to gain more insight on sorbent capacity, breakthrough and effect of temperature and moisture contents. Three sorbents were tested: sodium carbonate (Na_2CO_3), sodium oxide on alumina ($NaAlO_2$) and potassium carbonate (K_2CO_3). Of these sorbents, potassium carbonate proved to be the most effective in removing HCl without being affected by changes in temperature or moisture content. (Cavalli, 2016)

2.2.3 H_2S removal

H_2S is an extremely hazardous compound that is harmful to health, environment and equipment. Levels of H_2S above 100 ppm are described by the OSHA (Occupational Safety and Hazard Administration) as 'Immediately Dangerous to Life and Health'. (OSHA, 2005) H2S is also very harmful for equipment: it can poison catalysts downstream in the tar reformer, it can cause corrosion on turbines and it can poison the anode catalyst in a fuel cell. (Novochinskii, 2004)

The general process of removing H_2S is by flowing the contaminated gas through a reactor filled with a compound that can either chemically (chemisorption) react with or physically (physisorption) remove H_2S from the gas. Different types of sorbent and solvents exist for different operation conditions and applications.

H_2S removal from gas through physisorption has been widely researched with sorbents such as metal sorbents (Fe, Ni, Mg, Ca, Mn, Cu and Zn based) (Hepworth, 1993), zeolites such as FAU, LTA and MFI (Cosoli, 2008), activated carbon (Monteleone, 2011), ZnO based sorbents such as HTZ-5, HTZ-51 (Novochinskii, 2004), and even through biological processes (phototropic *C. Limicola* bacterium). (Syed, 2006) Generally, metal oxides are commonly used to remove sulphur from a gas at higher temperatures (300-500 °C).

Micoli et al. have performed H_2S removal tests with activated carbon modified with NaOH, KOH and Na_2CO_3 and zeolites modified with Cu and Zn. These modifications had improved the sorbents capability in adsorbing H_2S and improved breakthrough times, with activated carbon sorbent treated with Na_2CO_3 being the most effective. Overall, both the modified and non-modified activated carbon turned out to be more effective than the modified and non-modified zeolite sorbents. (Micoli, 2014)

In lower operating temperatures, liquid solvents can be used to absorb H_2S from a gas. Table 3 shows different solvents that are often used for cold H2S cleaning. (Abdoulmoumine, 2015)

Table 3 Overview of different widely used solvents for cold cleaning of H2S and their characteristics and operating conditions. (table extracted from Abdoulmoumine et al., 2015)

Solvent and process	Removal (%)	Process parameters	Quality of treated gas	Developed by	Remarks
MDEA (Chemical)	H_2S: 98-99 CO_2: +/-30	Temp: 30-35 °C (Ambient) Pr: <2.94 MPa	H_2S: 10-20 ppmv	Union carbide, UOP, Dow chemical, Shell	Lowest capital cost, moderate operating temperature, only limited physical COS absorption takes place
Selexol (Physical)	H_2S: 99 CO_2: variable	Temp: -7 to 4 °C Pr: 6.87 MPa	H_2S: <30 ppmv	Allied Chemical Corp., Union Carbide, UOP	Higher cost than MDEA but overall system cost including sulfur recovery (SR) process and tail gas treating (TGT) could be more cost effective
Rectisol (Physical)	H_2S: 99-99.9 CO_2: 98.5	Temp: -35 to -60 °C Pr: 8.04 MPa	H_2S: <0.1 ppmv CO_2: several mol% to few ppm	LINDE AG	Highest cost, a minimum concentration of the H_2S is required to maintain the activity of the catalyst, high selectivity for H_2S over CO_2, ability to remove COS

2.2.4 Tar removal

2.2.4.1 Tar definition and issues

The amount and type of tar found in syngas depends strongly on the type of fuel used and the temperature and oxygen levels during the gasification process. Elliot proposed a model that depicts the maturation of tars as a function of operating temperature. This model can be seen below in figure 10. (Elliott, 1988)

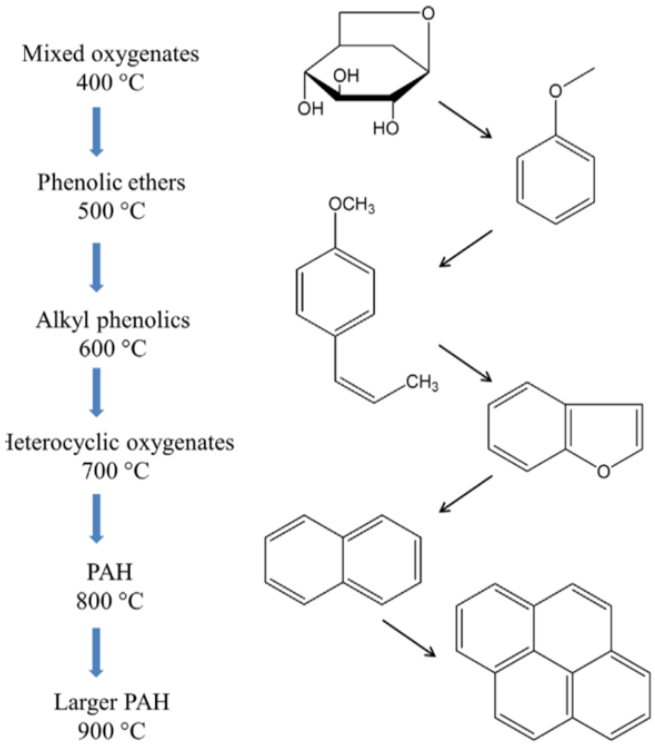


Figure 10 Tar maturation as a function of operating temperature. (Elliott, 1998)

The term 'tar' has been described in many different ways, based on for example its appearance or molecular weight. In 1998, during the EU/IEA/US-DOE meeting, a group of experts defined tar as all organic contaminants with a molecular weight higher than benzene. (Rajczykowski, 2016) . Another description of 'tar' that is acknowledged widely is: 'the condensable fraction of the organic gasification products and are largely aromatic hydrocarbons, including benzene'. (Guan, 2016) Based on appearance, several researchers have classified tars into three classes (table 4) (Palma, 2012) (Devi, 2005) (Milne, 1998)

Table 4 Tar classification based on molecular structures. (Palma, 2012) (Devi, 2005) (Milne, 1998)

Tar Class	Description
Primary	Low molecular weight oxygenated hydrocarbons such as levoglucosan, furfural and hydroxy acetaldehyde, produced at 400–700°C
Secondary	Phenolic and olefin compounds such phenol, cresol and xylene, produced at around 700–850°C
Tertiary	Complex aromatic compounds such as benzene, naphthalene, pyrene and toluene, produced at around 850–1000°C

Tar compounds are also described and classified based on its molecular weight (table 5). (Li, 2009) (Devi, 2005)

Table 5 Tar classification into 5 classes based on molecular weight. (table composed from Li (2009) and Devi (2005))

Tar class	Description
Class 1	GC undetectable heaviest tars which condense at high temperature and very low concentration
Class 2	Heterocyclic aromatic compounds which are high water solubility such as pyridine, phenol, cresols, quinoline, isoquinoline and dibenzophenol
Class 3	Light hydrocarbon aromatic compounds (1 ring) which do not cause a problem regarding condensability and solubility such as toluene, ethylbenzene, xylenes, styrene
Class 4	Light polyaromatic hydrocarbon compounds (2–3 rings) which condense at low temperature even at very low concentration such as indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
Class 5	Heavy polyaromatic hydrocarbon compounds (4–7 rings) which condense at high temperature at low concentration such asfluoranthene, pyrene, chrysene, perylene, coronene

Tars are considered an issue or a contaminate to syngas for a number of reasons associated with: 1) condensation, 2) formation of tar aerosols and 3) polymerization. (Vakalis, 2018) These are the main reasons that cause clogging up of the lines and tubes, de-activation of catalysts and a lower conversion of carbon which results in a lower efficiency. There is not a single general composition for biomass derived syngas. This is due to the many factors that influence the final gas composition. These factors include operating temperature, pressure, air feed, catalysts use, type of gasifier etc. In the figure (figure 11) below, a 'typical' tar composition that is derived from the gasification of biomass is shown. (Shen, 2013)

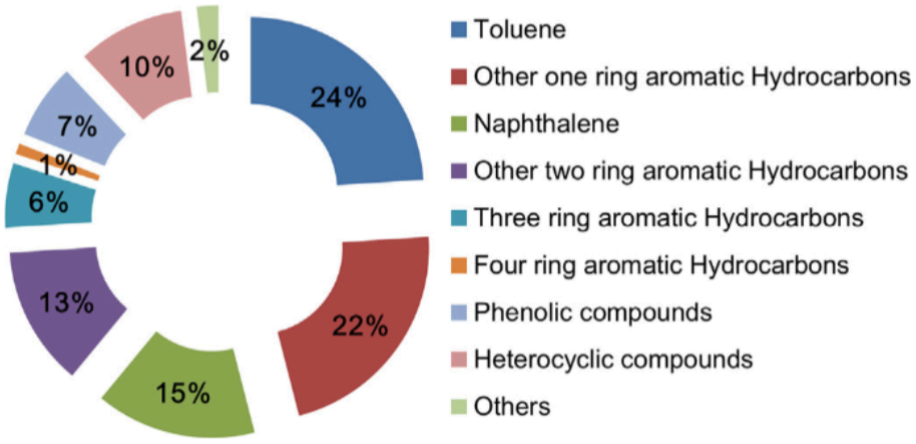


Figure 11 Typical tar composition of syngas derived from the gasification of biomass. (Shen, 2013)

These tar issues of polymerization and condensation also occur in an Internal Combustion Engine (ICE). In this process, the producer gas must be kept below 100 °C in order to keep the fuel density high and to remove the moisture in the gas. However, at these lower temperatures, tar begins to condensate and form a sticky residue. (Vakalis, 2018) A turbine can be run with higher temperature fuel and thus is less sensitive to the forming of a sticky residue due to tar condensation. However, at more than 400 °C, a dehydration reaction occurs which forms the tar in to a solid coke. This process is called 'coking' and it also responsible for the clogging of lines and tubes, as well as abrasion of downstream equipment. It can also deactivate certain tar catalysts. (Rios, 2018) The same issues occur in the solid oxide fuel cell operation. The tar vapor deposits on to the catalytic surface which reduces the reactive surface area until it becomes inactive completely. (Asadullah, 2014)

2.2.4.2 Cold and hot gas cleaning of tars

Cold gas cleaning

Tar cleaning or removal can be done in either low or high temperatures, resp. called the cold gas clean-up and the hot gas clean-up. In cold gas cleaning the working temperature of the syngas is usually around 300 °C or lower, and can be done either 'dry' or 'wet', depending on the gas cleaning equipment. In dry gas cleaning no water is used as a cleaning medium and the cleaning setup usually include a cyclone, sand filters, fabric and ceramic filters, particle separators and/or absorbers. On the other hand, in wet gas cleaning water is used the cleaning equipment include wet scrubbers, wet cyclones, and ESPs (electrostatic precipitators). As water is used in wet gas cleaning, it causes the syngas to cool down which is not favorable for the efficiency of the overall process. Since most of the contaminants are highly soluble in water, wet gas cleaning removes most of the tars in the gas. Still, some non-polar tars are less soluble in water and escape the wet cleaning.

In different works researchers clean the tar by combining wet and dry cleaning. In a paper by (Martínez, 2011), eucalyptus wood derived syngas was cleaned using a cyclone, heat exchanger and a bag house filter used managed to reduce tar contents in the syngas to <35 mg/Nm^3, but saw a low LHV of 4.6 MJ/Nm^3. In a study performed by (Margaritis, 2012), a cyclone, heat exchanger, chiller, demister, fine filter and venture scrubber were utilized and tar contents were reduced to 10 mg/Nm^3, but again with a low LHV of around 4.46 MJ/Nm^3. For continuous SOFC operation these concentrations of tars are still too high (table 1) and the low LHV and cold gas efficiency would reduce the overall efficiency, which make cold gas cleaning of tars a non-viable method for SOFCs. (Asadullah, 2014)

Hot gas cleaning

In hot gas cleaning, operating temperatures usually are higher than 300 °C. Compared to cold gas cleaning it is expected to yield higher efficiencies. (Aravind P. V., 2012) Hot gas filtration is one of the methods in hot gas cleaning and it relies on the physical separation of particles in the gas. Hot gas filters such as ceramic candle filters, as discussed in Chapter 2.2.1., are highly effective in removing particulate matters but not so for the removal of tars. At high temperatures tar volatiles remain in gas phase and easily escape the filter. Another disadvantage is that the filter can get clogged and thus create a pressure drop in the system. (Ashok, 2020) Therefore the use of a hot gas filter is not recommended as the only cleaning equipment, but rather in a combination with other hot gas cleaning methods. The other methods to remove tar compounds in hot gas operation are thermal cracking and catalytic reforming. (Asadullah, 2014) In thermal cracking, tar compounds are decomposed (reaction 13) at high temperatures ranging from 1000 °C to 1300 °C.

$$C_nH_m \rightarrow (m/4)CH_4 + (n\text{-}m/4)C \qquad \text{Thermal cracking} \qquad (13)$$

Although thermal cracking is highly effective in cracking tars, it is not a favorable method of removing tars because the reaction produces soot which is responsible for downstream clogging of lines and tubes. Another reason thermal cracking is less favorable is due to the fact that it requires the heating of the gas which reduces thermal efficiency and requires a higher air-to-fuel ratio to effectively crack tars which reduces the energy content in the gas. Tar can be catalytically reformed through partial oxidation, steam reforming, dry reforming. These mechanisms are described below in Chapter 2.2.4.3.

2.2.4.3 Catalytically tar reforming

There are two ways tars are reformed catalytically in a gasification system, namely through primary or secondary catalysts. Primary catalysts are added directly to the fuel, either by mixing the catalyst with the fuel or by wet impregnation of the fuel. Their primary function is to reduce tar content in the syngas. The secondary catalysts are also referred to as guard bed catalysts and usually is placed in a downstream reactor. The secondary catalysts are more effective than the primary catalysts mainly because of the fact that the secondary catalysts can react in different (less extreme) operating conditions than in the gasifier. Another added benefit of using secondary catalysts over primary catalysts is that secondary catalysts not only reduce tar contents, but also actively reforms methane and hydrocarbons to an increased hydrogen production, which raises the energy content of the syngas. (Sutton, 2001)

Catalysts

Researchers have found many catalytic compounds that can be used for tar reforming. The use of catalysts is potentially more attractive as efficiency and heating value losses are minimal as no additional energy is required. Also, with catalysts no tarry waste streams are produced. (Aravind P. V., 2012) When deciding which catalysts to use in a process to remove tar from (syn)gas, one should consider certain criteria for comparison between catalysts. For example, Suton et al. proposed that the catalyst must:

- be effective in tar removal;
- be effective in methane reforming;
- provide an optimal syngas ratio;
- be resistant to deactivation;
- be regenerated easily;
- be strong;
- be inexpensive.

Nowadays many catalyst materials exist and can be divided into the following nine categories: 1) iron ore catalysts, 2) olivine catalysts, 3) clay mineral catalysts, 4) calcined rock catalysts, 5) alkali-based catalysts, 6) activated alumina catalysts, 7) transition metal-based catalysts, 8) FCC's and 9) char catalysts. (Sutton, 2001)

The most frequently used catalysts include dolomite, Al_2O_3, olivine and zeolites. Out of these catalysts dolomite and olivine are available in excess quantities and lower costs and thus are more favourable. (Guo, 2018) However, due to coke formatting these catalysts can be deactivated faster than other catalysts. (Di Felice, 2010) Dolomite is a magnesium ore that usually contains around 15 wt.% MgO, 35 wt.% CaO and 45 wt.% CO_2 and traces of Fe_2O_3, Al_2O_3 and SiO_2.

Catalytic mechanisms

Reforming tar is done through one of three catalytic mechanisms: 1) Partial oxidation, 2) steam reforming and 3) dry reforming. Their reaction mechanisms are described below. Tars are described as the general hydrocarbon formula C_nH_m. (Richardson, 2015)

$C_nH_m + (n/2)O_2 \rightarrow nCO + (m/2)H_2$	Partial oxidation	(14)
$C_nH_m + nH_2O \rightarrow (m/2+n)H_2 + nCO_2$	Steam reforming	(15)
$C_nH_m + nCO_2 \rightarrow 2nCO_2 + (m/2)H_2$	Dry reforming	(16)

These mechanisms all have been researched extensively in the past decades and each have their advantages and disadvantages. Partial oxidation of biogas has proven to be able to reduce and convert primary tars at temperatures above 900 °C. (Ahrenfeldt, 2013).

Generally, tar is removed by steam reforming due to it being more advantageous than the other catalytic mechanisms. In this process, the hydrocarbons are dehydrogenated. Carbon is deposited onto the catalysts active sites and is gasified according to reactions (2), (3), and (4) (see Chapter 2.1.2). (Wang T. J., 2005) This process produces extra CO and is required to keep the activity of the catalyst. (Świerczyński, 2007) Some of the advantages of this mechanism are: 1) composition of the syngas can be tweaked, 2) the steam can be added for complete tar reforming and 3) the temperatures of the catalyst reactor and the gasifier can be integrated which positively affects the thermal efficiency of the system. (Dayton, 2002)

2.3 Syngas to electricity

The last step in turning biomass into electrical energy is the fuel cell. A fuel cell is an electrochemical device that can produce (electrical) energy from (a mixture of) hydrogen, carbon monoxide and methane. Fuel cells that are operated under high pressures can be combined with gas turbines to achieve high efficiencies. (Aravind, 2009) Unlike batteries, fuel cells don't store the chemical energy but instead is fueled which allows for long operation times. Hydrogen and hydrocarbon-rich fuels can be used in this process. Fuel cells have a broad range of applications, ranging from transport (hydrogen cars and busses) to portable and stationary energy generation. Fuel cells have many advantages over conventional energy generation methods: (Larminie, 2003)

- Can reach higher efficiencies (35-55%) compared to conventional gas and diesel engines.
- Consists of a few moving parts which makes this technology less prone to (high) maintenance.
- Friendlier to the environment as it does not require the burning of fossil fuels and its only by-product is water.
- Possibility of decentralized power generation and power generation in off-grid locations.

Many different fuel cells exist that utilize different operating conditions, fuels and electrolytes. However, their basic working principle is the same. This general working principle is described below in Chapter 2.3.1., then, in Chapter 2.3.2., the different types of fuel cells are described and compared.

2.3.1 Working principle

In order for a fuel cell to generate electricity, it relies on oxidation and reduction reactions and requires a constant flow of an oxidant (air) to the positive side (referred to as cathode side) and a fuel on the negative side (referred to as anode side), an electrolyte and an external circuit through which electrons can move. (Aravind P. V., 2012) (Larminie, 2003) This principle is illustrated below in figure 12.

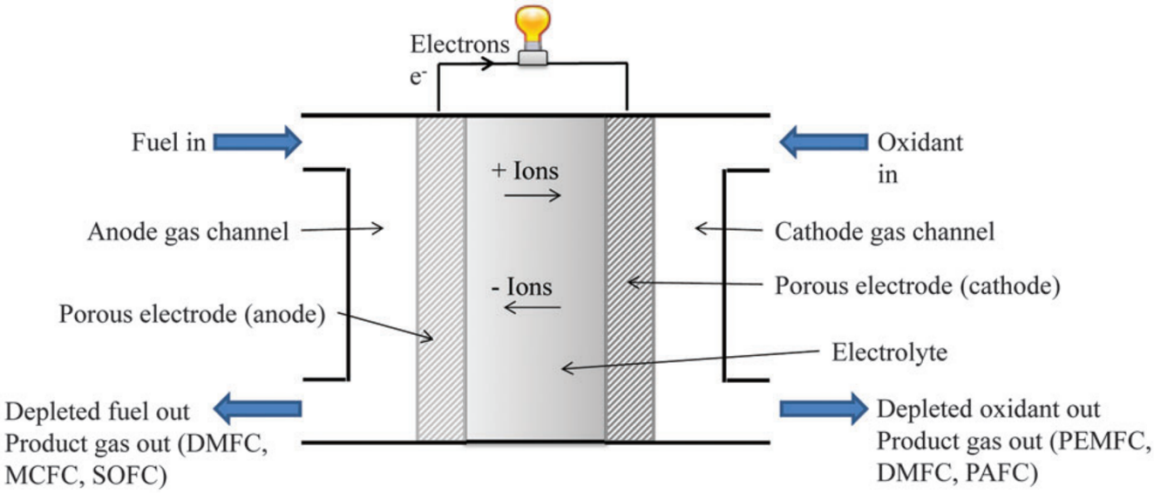


Figure 12 Working principle of a fuel cell, consisting of an anode and cathode side, an electrolyte and an external circuit. (Linares, 2014)

At the anode inlet a fuel is injected and oxidized, while at the cathode side air is injected and reduced. The electrons and ions are separated through a semi-permeable electrolyte and an external circuit where current is drawn from by connecting it to a load. (Linares, 2014). Each type of fuel cell relies on different redox reactions. These (half-)reactions that produce electrons are elaborated more on in Chapter 2.3.2.

One of the key differences between the different fuel cell types comes from the choice of electrolyte. An electrolyte is a semi-permeable that only allows certain ions to pass through. (Larminie, 2003) This separation of electrons and protons is critical for fuel cell operation and can greatly determine the electrical efficiency of the process. Ideally, an electrolyte should 1) be stable at extreme operating conditions, 2) be a good ion conductor, 3) have low electrical conductivity (electronically insulating ideally), 4) be compatible with the electrodes and 5) be gas tight 6) be flexible in terms of fuels it can operate with and 7) be economically attractive (for possible commercial use). (van der Kleij, 2012) (Sudhakar, 2018)

2.3.2 Types of Fuel Cells

There are several types of fuel cells available, each with different reaction mechanisms, used for different specific applications. The table below shows the most commonly used fuel cells and some of their properties and applications (table 6).

Table 6 Types of Fuel Cells and their specific properties (Haile, 2003) (FuelCellToday, 2012) (Larminie, 2003)

Fuel Cell Type	Temp. (C *)	Fuel	Electrolyte	Mobile Ion
Proton Exchange Membrane FC	70 – 110	H_2 CH_3OH	Sulfonated polymers	H^+
Direct Methanol FC	60 – 130	CH_3OH (Liquid methanol)	Polymer membranes	H^+
Alkali FC	100 – 250	H_2	KOH (aq)	OH^-
Phosphoric Acid FC	150 – 250	H_2	H_3PO_4	H^+
Molten Carbonate FC	500 – 700	CO Hydrocarbons	$(Na,K)_2CO_3$	CO_3^{2-}
Solid Oxide FC	700 – 1000	CO Hydrocarbons	$(Zr,Y)_{O2-\delta}$	O^{2-}

PEMFC – Proton Exchange/Electrolyte Membrane Fuel Cells

As the name suggests, in this type of fuel cell the ions that are transferred (exchanged) through the electrolyte are protons. The electrolyte usually is a solid polymer and is often sulfonated. One of the main advantages over other fuel cell types is that it operates are low temperatures (70-110 °C) which makes it have a short start-up time and viable to be used electronic (handheld) devices, bikes and other transportation. (Haile, 2003) The PEMFC is usually fueled with hydrogen, however different variations exist: in a Direct Formic Acid Fuel Cell (DFAFC) formic acid (HCOOH) is used and in a Direct Ethanol Fuel Cell (DEFC) ethanol. (Suraparaju, 2019) Below, in figure 13, the general principle of a PEMFC is illustrated (assuming hydrogen is used as the fuel).

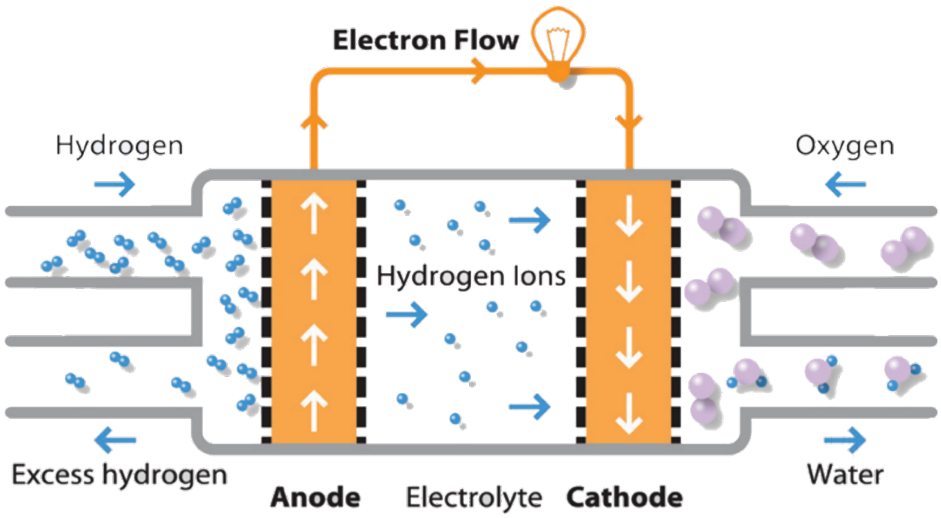


Figure 13 Schematic overview of the working principle of a Proton Exchange Membrane Fuel Cell (PEMFC). (FuelCellToday, 2012)

The chemical reactions that are required for PEMFC operation are:

$H_2\ (g) \rightarrow 2H^+\ (aq) + 2e^-$ [Anode] (16)

$½\ O_2\ (g) + 2H^+ + 2e^-\ (aq) \rightarrow H_2O\ (l)$ [Cathode] (17)

$H_2\ (g) + ½\ O_2\ (g) \rightarrow H_2O\ (l)$ [Overall] (18)

DMFC – Direct Methanol Fuel Cells

The DMFC is regarded as a novel and innovative power generating device. Similar to the PEMFC and DEFC, a DMFC utilizes liquid methanol as a fuel. At the anode side, the liquid methanol is dissolved in water in a reaction that produces hydrogen and which is transferred over the polymer electrolyte to the cathode side. Having a low operating temperature, the DMFC has a quick start-up time and is used in electronic (handheld) devices. (Suraparaju, 2019) An added benefit to using methanol as a fuel is that at the anode side no reformer is needed to attract the hydrogen, which makes it cost less to operate. The working principle of a DMFC is illustrated below in figure 14; on the cathode side it is similar to a PEMFC, only at the anode side methanol is used and carbon dioxide is produced.

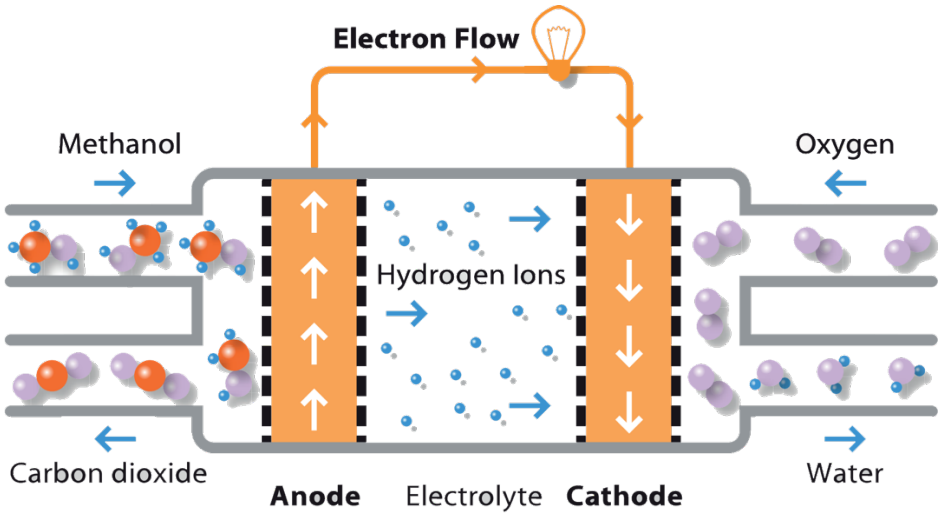


Figure 14 Schematic overview of the working principle of a Direct Methanol Fuel Cell (DMFC). (FuelCellToday, 2012)

The chemical reactions that are required for DMFC operation are:

$CH_3OH\ (l) + H_2O\ (l) \rightarrow 6H^+\ (aq) + 6e^- + CO_2\ (g)$ [Anode] (19)

$\frac{3}{2}\ O_2\ (g) + 6H^+\ (aq) + 6e^- \rightarrow 3H_2O\ (l)$ [Cathode] (20)

$CH_3OH\ (l) + \frac{3}{2}\ O_2\ (g) \rightarrow 2H_2O\ (l) + CO_2\ (g)$ [Overall] (21)

PAFC – Phosphoric Acid Fuel Cells

PAFC's utilize hydrogen as fuel and highly concentrated (>95%) liquid phosphoric acid (H_3PO_4) as the electrolyte to conduct hydrogen ions over to the cathode side. Due to its long and reliable operating times without maintenance, and its high resistances to carbon dioxide poisoning, these type of fuel cells are widely used as stationary power generators of up to 400 kW. (FuelCellToday, 2012) Due to higher operating temperatures (170-210 °C), cogeneration of hot water and electricity is possible which boosts efficiencies tremendously. Since it only operates on hydrogen, the fuel flexibility is less. Naturel gas can be reformed on-site to produce the required hydrogen for power generation, but this increases complexity and costs of the system. (Suraparaju, 2019) Also, PAFC's make use of platinum catalysts which are costly and non-friendly for the environment. Below, in figure 15, the working principle of a PAFC system is depicted.

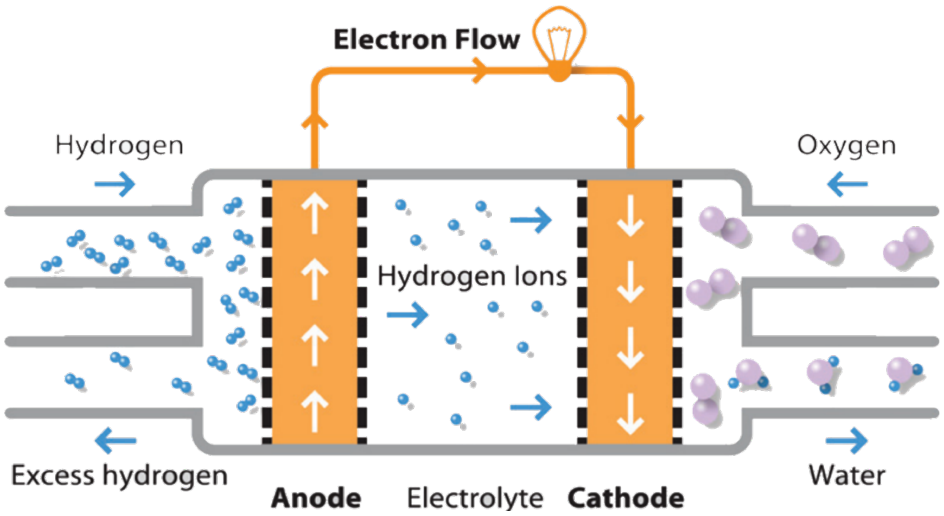


Figure 15 Schematic overview of the working principle of a Phosphoric Acid Fuel Cell (PAFC). (FuelCellToday, 2012)

The chemical reactions that are required for DMFC operation are:

$$2H_2\,(g) \rightarrow 4H^+\,(aq) + 4e^- \qquad \text{[Anode]} \qquad (22)$$

$$O_2\,(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(l) \qquad \text{[Cathode]} \qquad (23)$$

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l) \qquad \text{[Overall]} \qquad (24)$$

AFC – Alkaline Fuel Cells

In an AFC, the electrolyte is a KOH (potassium hydroxide) liquid solution, as opposed to solider polymer electrolyte in other types of fuel cells. This type of fuel cell is capable of reaching up to 70% efficacy and also has the benefits of low temperature and quick start-up time. (Suraparaju, 2019) The main disadvantage is that this process is highly sensitive to poisoning from carbon dioxide and causes a shorter life span. As a consequence, the

air used at the cathode inlet must be free of carbon dioxide which requires an extra step of purification. (Gülzow, 1996) These benefits led the employment of this type of fuel cell in NASA's space missions and experiments. Figure 16 depicts the working principle of an AFC. (Gasik, 2008)

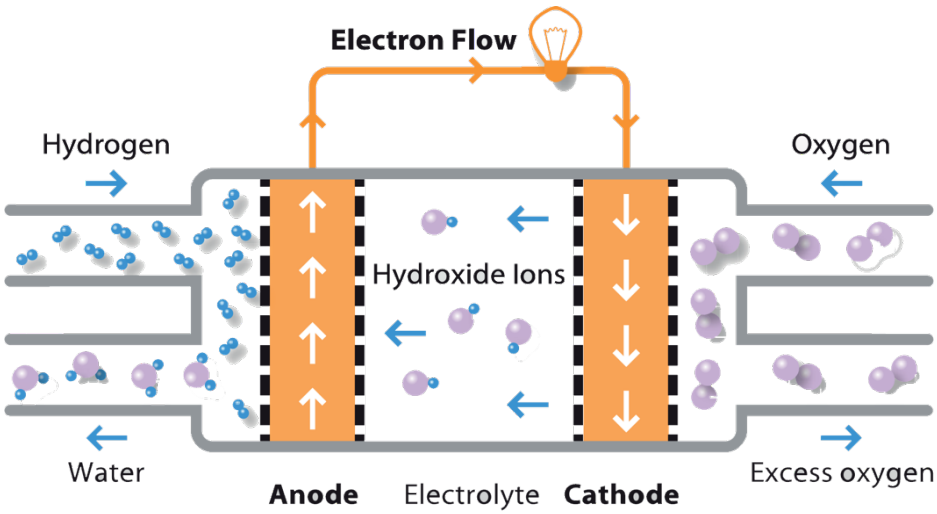


Figure 16 Schematic overview of the working principle of an Alkaline Fuel Cell (AFC). (FuelCellToday, 2012)

The chemical reactions that are required for AFC operation are:

$$H_2\,(g) + 2OH^-\,(aq) \rightarrow 2H_2O\,(l) + 2e^- \qquad \text{[Anode]} \qquad (25)$$

$$\tfrac{1}{2}\,O_2\,(g) + H_2O\,(l) + 2e^- \rightarrow 2OH^-\,(aq) \qquad \text{[Cathode]} \qquad (26)$$

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l) \qquad \text{[Overall]} \qquad (27)$$

SOFC – Solid Oxide Fuel Cells

The Solid Oxide Fuel Cell (SOFC) can reach high electrical efficiencies of 50-60% and due to the high operating temperatures, the heat can be recuperated to increase overall efficiency up to 80-85%. The SOFC operates at much higher temperatures than other fuel cells. These high temperatures of around 700 to 1000 °C are required for an optimal electron conductivity of the electrolyte. A commonly used material for fuel cell electrolytes is zirconia oxide (ZrO_2) stabilized with yttria to form a solid ceramic material named Yttria-Stabilized Zirconia (YSZ). (Chen, 2003) Oxygen enters the cell from the cathode side and oxidizes to generate oxygen ions that are conducted through the electrolyte to the anode side. Depending on the fuel (H_2 or syngas), these oxygen ions at the anode side then react with the fuel which generates electrons, as well as carbon dioxide and H_2O as byproducts. (Haile, 2003) Figure 17 shows the working principle of a SOFC.

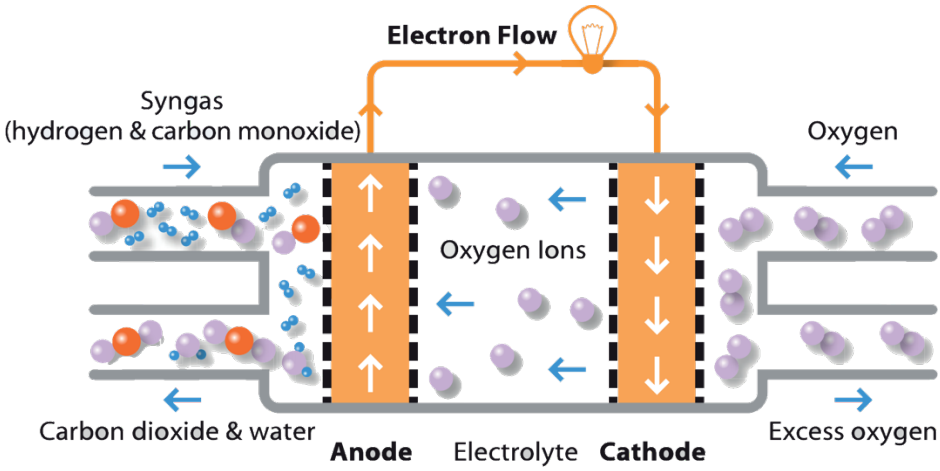


Figure 17 Schematic overview of the working principle of a Solid Oxide Fuel Cell (SOFC). (FuelCellToday, 2012)

The main advantages include high efficiencies, great reliability and the ability to internally reform natural gas and syngas. Cavalli et al. (2017) successfully fed HCl and toluene (as a model representative for tars) to a SOFC cell and found that quantities up to 8.5 g/nM^3 of toluene have negligible effect cell performance. However, HCl presence does seem to hamper the reforming of toluene. Drawbacks of the SOFC systems include cracking of the components at high temperatures and being prone to chlorine and sulphur poisoning.

The chemical reactions that are required for SOFC operation are:

$$H_2\,(g) + O^{2-}\,(aq) \rightarrow H_2O\,(l) + 2e^- \qquad \text{[Anode – } H_2\text{]} \quad (28)$$

$$CO\,(g) + O^{2-}\,(aq) \rightarrow CO_2\,(g) + 2e^- \qquad \text{[Anode – CO]} \quad (29)$$

$$\tfrac{1}{2}\,O_2\,(g) + 2e^- \rightarrow O^-\,(aq) \qquad \text{[Cathode]} \quad (30)$$

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l) \qquad \text{[Overall]} \quad (31)$$

Molten Carbonate Fuel Cells – MCFC

As the name suggests, MCFC's utilize carbonates that melt at higher temperatures (above 600 °C). At these high temperatures, the molten magnesium or sodium carbonates interact with the $LiAlO_2$ matrix and allow for carbonate ions (CO_3^{2-}) to transport across from the cathode to the anode side (figure 18). Oxygen and carbon dioxide enter the cathode side and react with the electrons to produce carbonate ions. These carbonate ions then interact with the syngas fuel to generate CO_2, H_2O and an electron flow. As with other fuel cells that operate at elevated temperatures, this heat can be harvested to increase overall efficiency of the system (combined heat and electricity). Also, MCFC's can directly use syngas as a fuel and are less prone to carbon dioxide poisoning than low temperature fuel cells. A downside of using MCFC's is that its electrolyte causes corrosion in the system and the high temperatures wear the components down faster than at low temperatures.

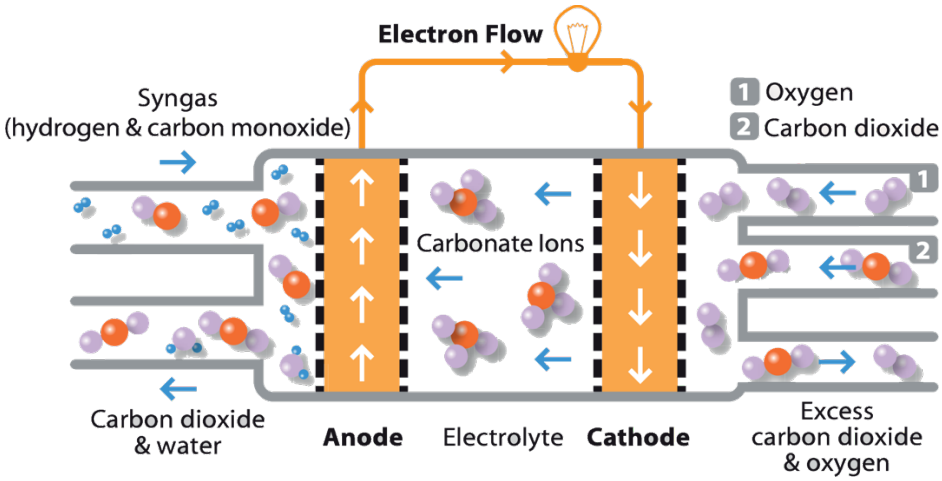


Figure 18 Schematic overview of the working principle of a Molten Carbonate Fuel Cell (MCFC). (FuelCellToday, 2012)

The chemical reactions that are required for MCFC operation are:

$H_2\ (g) + CO_3^{2-}\ (aq) \rightarrow CO_2\ (g) + H_2O\ (l) + 2e^-$ [Anode] (32)

$O_2\ (g) + CO_2\ (g) + 2e^- \rightarrow CO_3^{2-}\ (aq)$ [Cathode] (33)

$H_2\ (g) + O_2\ (g) \rightarrow H_2O\ (l)$ [Overall] (34)

2.4 Chapter summary

The process of converting biomass to electricity is described in this chapter. Here it is divided into three stages: 1) gasification of biomass, 2) cleaning of the raw syngas and 3) the electrochemical conversion from syngas to electricity via fuel cells:

1) Biomass is fed into the gasifier where biomass is introduced to high temperatures. Under these conditions the biomass starts breaking down according to different chemical steps, which are greatly influenced by the composition of the fuel, the operating temperatures and the gasification agent used. The gasification of biomass materials produces a raw syngas that, after cleaning, can be used to produce electricity.

2) The raw syngas from the gasifier must be cleaned first before it can be used as a fuel for electricity generation. The main contaminants are chlorine, sulphur, tar compounds and particulate matter. The gas cleaning unit contains several reactors, which each are designed to remove a specific contaminant. In this system, particulate matter is removed with a ceramic candle filter, chlorine with a K2CO3 sorbent, sulphur with a ZnO based sorbent and tar with a nickel-based catalyst.

3) Once cleaned, the syngas can be fed to a fuel cell. A fuel cell is an electrochemical device which converts chemical energy into electrical energy. The different types of fuel

cells and their advantages and disadvantages are elaborated on. However, in all types of fuel cells the general working principle is the same: the fuel is introduced at the negative side (the anode) where it is oxidized, while at the positive side (the cathode) air is fed and reduced. The anode and cathode side are separated by a semi-permeable barrier, the electrolyte, which allows for ion transport. Then, current is drawn via an external circuit.

3. Methodology

In this chapter the methodology of sampling of the contaminants is described in greater detail. The contaminants to be sampled and analyzed are HCl, H_2S and tar compounds. The objective of the Gas Cleaning Unit is to clean the syngas from contaminants so that the produced gas can be fed to a SOFC without damaging and poisoning the fuel cell. The maximum concentrations of contaminants for the inlet stream for the fuel cell can be found below in table 7.

Table 7 Maximum allowed contaminant concentrations to be fed to the SOFC.

Contaminant	Maximum concentration
Chlorine (HCl)	< 5 ppm vol.
Sulphur (H2S)	< 1 ppm vol.
Particulate matter	0.1 mg/Nm^3
Tar compounds	< 1 ppm

A sampling train is built to sample the gas that is produced from the gasifier and measure its composition and the concentration of the main contaminants (HCl, H_2S and tar) at different locations of the GCU stream. HCl and H_2S samples are analyzed in TU Delft, while tar samples are analyzed by the Netherlands Organization for Applied Scientific Research (ECN/TNO).

3.1. Contaminants

HCl and H_2S sampling

HCl and H_2S were sampled through the use of gas bubbling bottles (impingers) and liquid absorbers. For H_2S an impinger bottle filled with a Zinc Acetate solution will act as the liquid absorber for sulphur. The liquid absorber for HCl is water, since HCl is highly soluble in water. The second method of measuring H_2S and HCl is via Dräger tubes. These methods are described below in detail. In table 8 an overview of the chemical and physical properties of HCl and H_2S is given.

Table 8 Compound summaries for HCl and H2S (data gathered from PubChem).

	H_2S	HCl
Synonyms	Hydrogen Sulphide, Hydro sulfuric acid, sulfane	Hydrogen chlorine, Hydrochloric acid, Muriatic acid
Boiling point	- 60.2 °C	- 85.1 °C
Melting point	- 85 °C	- 114.2 °C
Mol. Weight	34.076 g/mol	36.458 g/mol
Vapor pressure	20 ATM at 25.5 °C	40.5 ATM at 25 °C
Appearance	Colorless gas	Clear or slightly yellow

Vapor Density	1.190 (air = 1.0)	1.268 (air = 1.0)
Molecular Formula	H_2S	HCl
Odor	Offensive rotten egg smell	Pungent and Irritating.
Solubility	Soluble in alcohol and water	Soluble in water, ethanol and methanol

Method 1: Sampling through gas bubbling

This method is used to sample both H_2S and HCl and the working principle is the same for HCl as it is for H_2S sampling, only the absorbing liquids differ. The gas to be sampled is run through a set of two impinger bottles which contain an absorbing liquid, which captures the contaminant. For HCl the absorbing liquid is deionized water: syngas will pass two 100mL impinger bottles filled with 30 mL deionized water. The schematic of the HCl sampling line can be found below in figure 20.

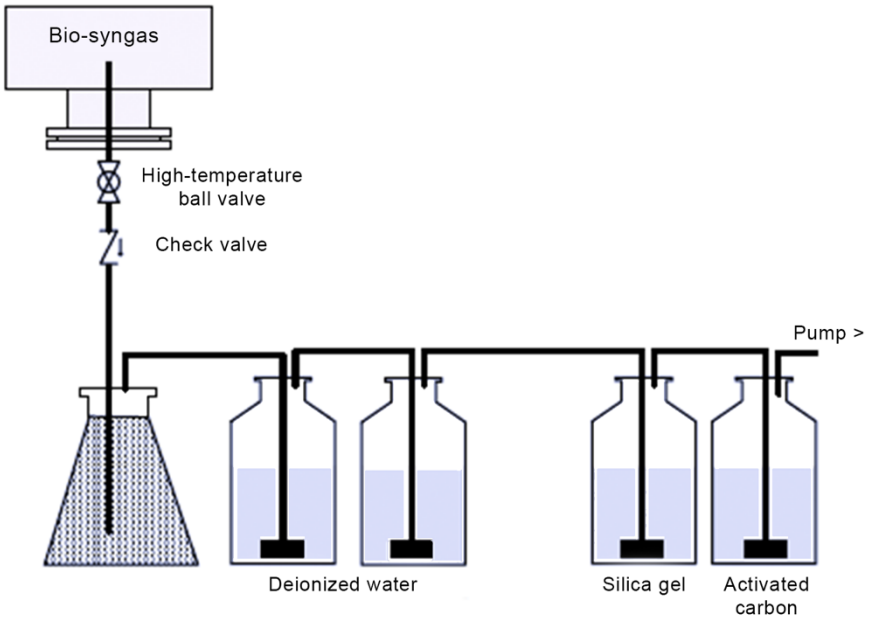


Figure 19 Schematic overview of HCl sampling with deionized water.

The flue gas first flows through a bottle containing a wool filter, to remove tars from the gas. The tar wool filter will be kept at 150 °C.

Afterwards, the syngas flows through the two bottles with deionized water, which captures chlorine. A second impinger bottle is placed to capture the chlorine that may not be captured by the first bottle even though it is expected, from previous measuring campaigns, that the first impinger bottle captures almost all chlorine. The calculated bubbling time is set to 30 minutes for both HCl and H_2S to ensure enough sulphur and chlorine is captured at each of the sampling points to be able to detect it with the respective analysis techniques for H_2S and HCl.

Finally, the gas passes two bottles containing silica gel and active carbon to remove moisture and contaminants that could damage the pump.

For capturing sulphur through gas bubbling, a similar sampling is used, but with a different absorbing liquid. The liquid to capture sulphur is a 2 g/L Zinc Acetate solution.

It is important to understand the chemical characteristics in order to effectively sample and analyze sulphur. H_2S is a weak acid that dissociates according to reaction (35) and (36) below.

$$H_2S \rightarrow H^+ + HS^- \qquad [K_{S1} = 1.1 * 10^{-7}] \qquad (35)$$
$$HS^- \rightarrow H^+ + S^{2-} \qquad [K_{S1} = 1.0 * 10^{-14}] \qquad (36)$$

Often NaOH and KOH are used as bubbling liquids, as they are strong bases in which H_2S can easily dissociate and thus be retained in. However, this method only works so long the pH of the solution stays above 8. This has proven to be an obstacle in bio-syngas sampling, as usually the gas contains up to $20\%_{vol}$ of CO_2. Just like H_2S, CO_2 will act as a weak acid (reaction 37) and in turn reduces the pH levels of the solution to low levels in which NaOH and KOH will lose their potential to retain sulphur. (Zeisler, 2010)

$$CO_2\ (aq) + 2H_2O \rightarrow HCO_3^- + H_3O^+ \qquad (37)$$

To stop this negative influence of CO_2, a zinc acetate solution is used instead of KOH or NaOH. The zinc acetate solution reacts with H_2S according to the following reaction mechanism (reaction 38-41). (Zeisler, 2010)

$$Zn(CH_3COO)_2 + H_2O \rightarrow Zn^{2+} + 2CH_3COO^- + H_2O \qquad (38)$$
$$H_2S\ (aq) + H_2O \rightarrow HS^- + H_3O^+ \qquad (39)$$
$$HS^- + H_2O \rightarrow S^{2-} + H_3O^+ \qquad (40)$$
$$Zn^{2+} + S^{2-} \rightarrow ZnS\ (s) \qquad (41)$$

The setup used to capture H_2S through gas bubbling can be found below in figure 20.

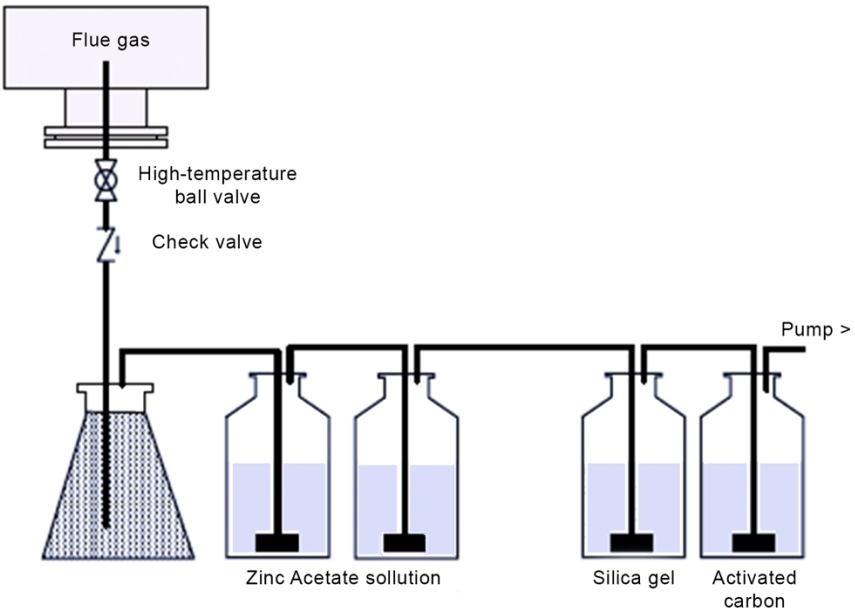


Figure 20 Schematic overview of H_2S sampling with a Zinc acetate solution.

Method 2: Dräger Tubes

The second method to measure the amount of H_2S and HCl in the syngas is done using Dräger tubes (figure 21). Dräger tubes glass tubes can measure the presence of a certain compound by allowing gas to flow through the tube which is filled with a compound that reacts with the contaminant and which produces a certain color. Measurement indicators on the glass tube can be read to show how much contaminant is in the gas. In order to suck the gas from the mainline to the sample line to flow it through the tube a Dräger Accuro hand pump is used (see figure 21 below). With each stroke of the hand pump it sucks 100 mL of gas through the tube. Depending on the type of tube, different number of strokes are required.

Figure 21 Several types of Dräger Tubes and the Dräger Accuro hand pump.

In order to measure gas samples directly from the flue gas with Dräger tubes, the tube is integrated in the sampling line. A handpump (Dräger Accuro) is used to overcome the pressure difference. In between the sampling point and the Dräger tube an impinger bottle containing a H_2SO_4/Isopropanol solution is placed. The isopropanol captures tar compounds that are in the flue gas. This is required as Dräger tubes are not designed to work with tars and are most likely to clog up the tube and give inaccurate measurements. However, isopropanol also captures a portion of the sulphur, which means that the Dräger tube would not measure all the sulphur in the gas. To overcome this issue, a 30% H_2SO_4 solution was added to the isopropanol in a 50:50 ratio. The sampling setup with Dräger tubes can be found below in Figure 22.

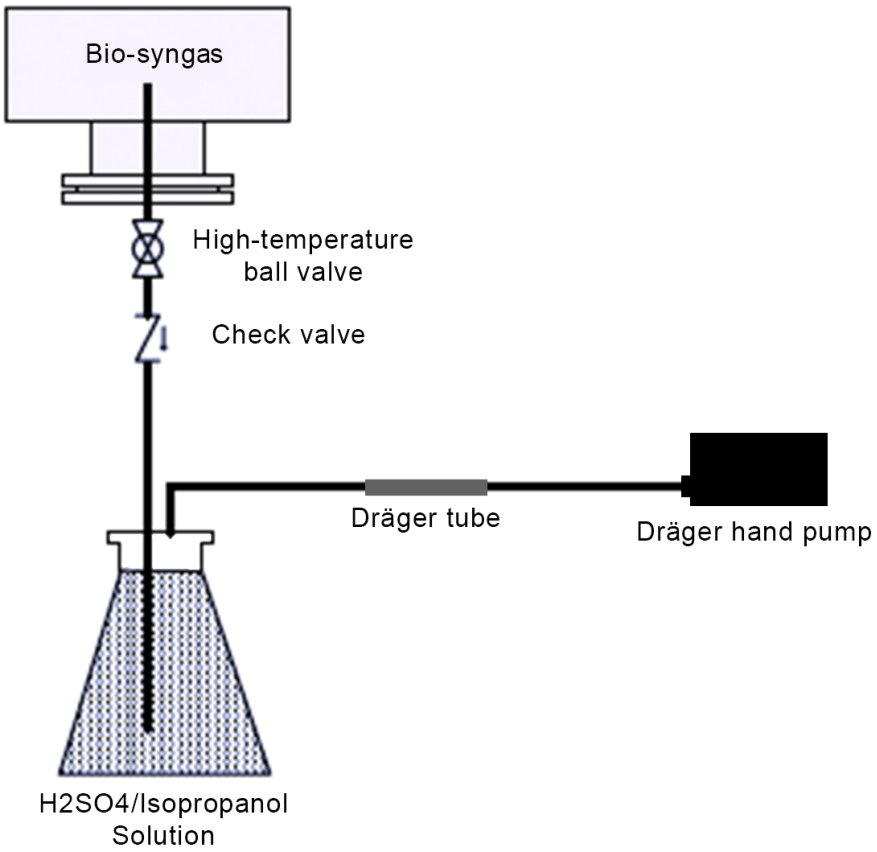


Figure 22 Schematic overview of sampling via Dräger tubes with a H2SO4/Isopropanol solution.

Usually this type of measurements is done in systems which have a pressure in the main line that is above atmospheric pressure and thus the hand pump can provide enough Net Positive Suction Head (NPSH). However, in this setup, the gas in the mainline is at under pressure (approx. 0.8 ATM). This may create a problem as the hand pump may not generate sufficient suction (and even air from the environment can enter the mainline). To make sure we can have reliable measurements with the Dräger Tubes, a side test was performed (test details and results in Chapter 3.1.1.) to see if the hand pump could suck the gas from a line that is below atmospheric pressure.

Another problem that occurred was that the isopropanol liquid through which the gas bubbles before entering the Dräger tube captures (some of the) sulphur passing through it. The gas is bubbled through isopropanol to clear the syngas from tars that will clog up the Dräger tube. However, if some of the sulphur is captured by the isopropanol, a lower value than the actual concentration would be measured from the Dräger tube and thus this method would not guarantee accurate measurements. In the same test described in Chapter 3.1.1. a different proposed solution was tested to see if it would stop capturing sulphur.

3.1.1. Side test Dräger Tubes

Before using Dräger tubes as a method of measuring sulphur and chlorine concentrations, proposed solutions for two issues had to be tested and validated: 1) can the hand pump suck gas from a line that is below atmospheric pressure and 2) does introducing sulphuric acid (H_2SO_4) in the isopropanol mixture allow the sulphur to not be captured by the liquid? In order to test this, a simple test rig has been set up. A schematic and an actual picture of the setup and can be found in figure 23 and 24 below.

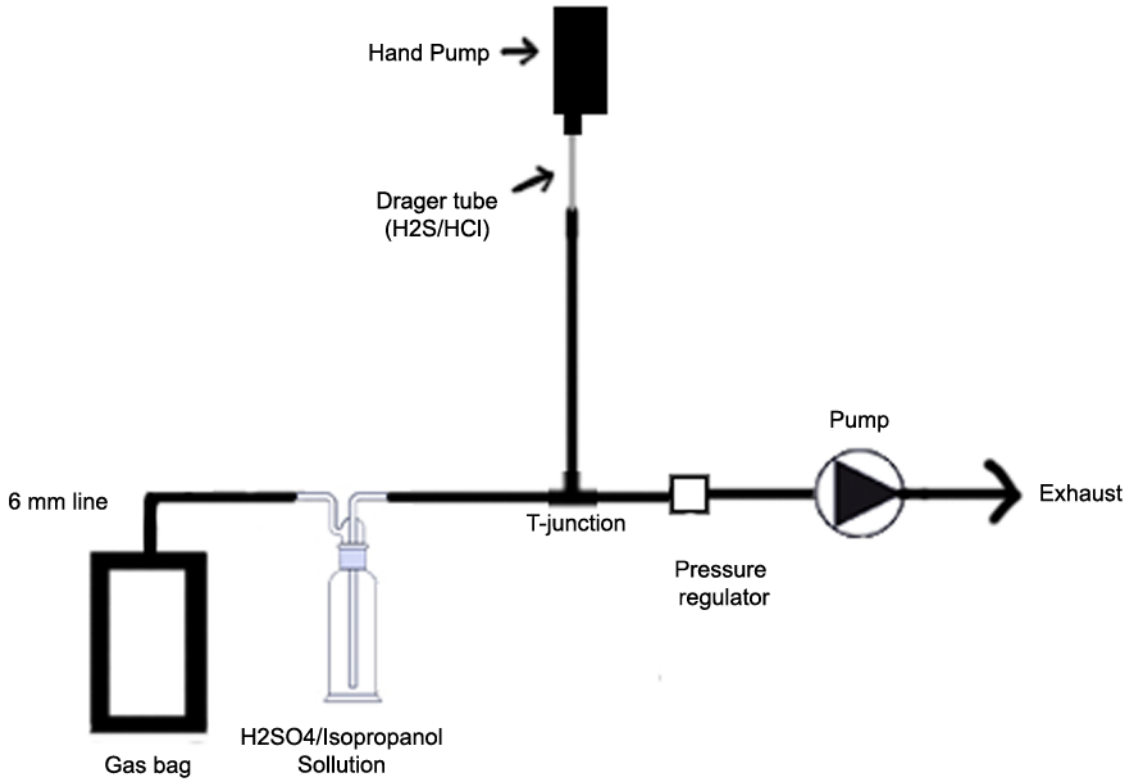


Figure 23 Schematic of the Dräger tube test setup.

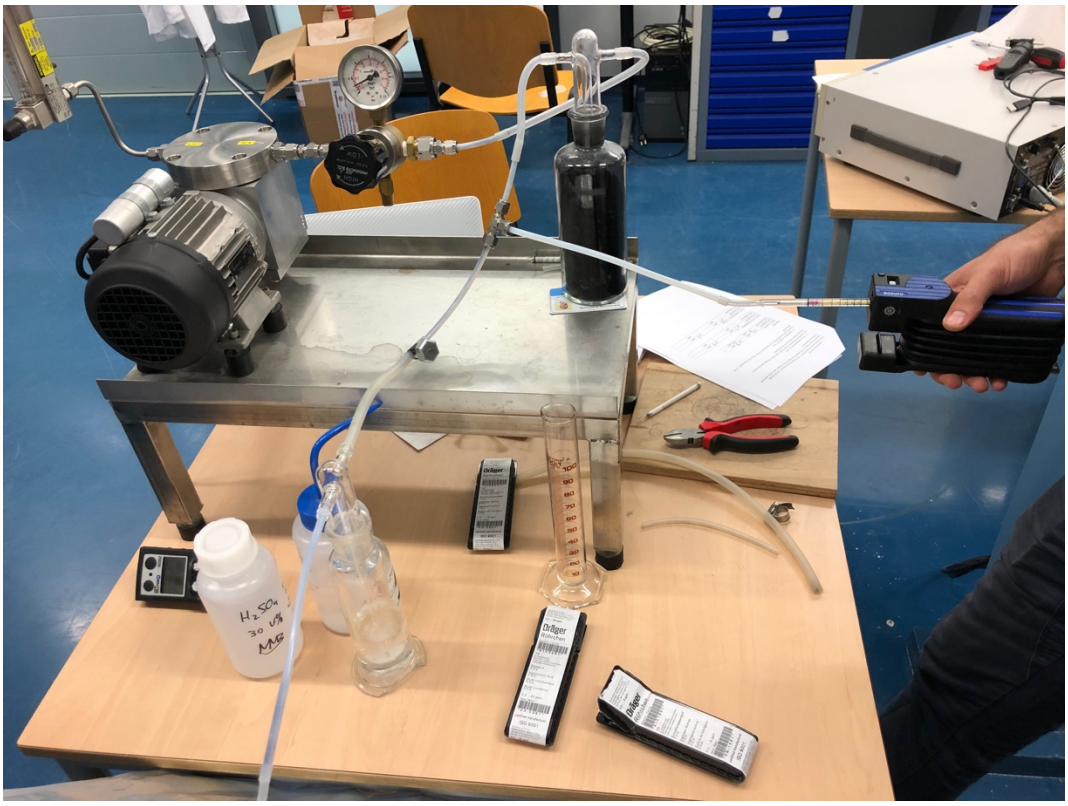


Figure 24 Picture of the test setup with the pump on the left, the hand pump right of the T-junction and the sulphur containing gas bag in the bottom.

Two gas bags were prepared containing different amounts of sulphur. The first bag was prepared with 6 ppm H_2S and the second bag was prepared with 1 ppm H_2S. The pressure was regulated to be around 0.6 ATM in the line. The H_2SO_4 mixture used was a 30% H_2SO_4 in water solution in 50:50 ratio with isopropanol. The results of the measurements can be found below in figure 25 and table 9.

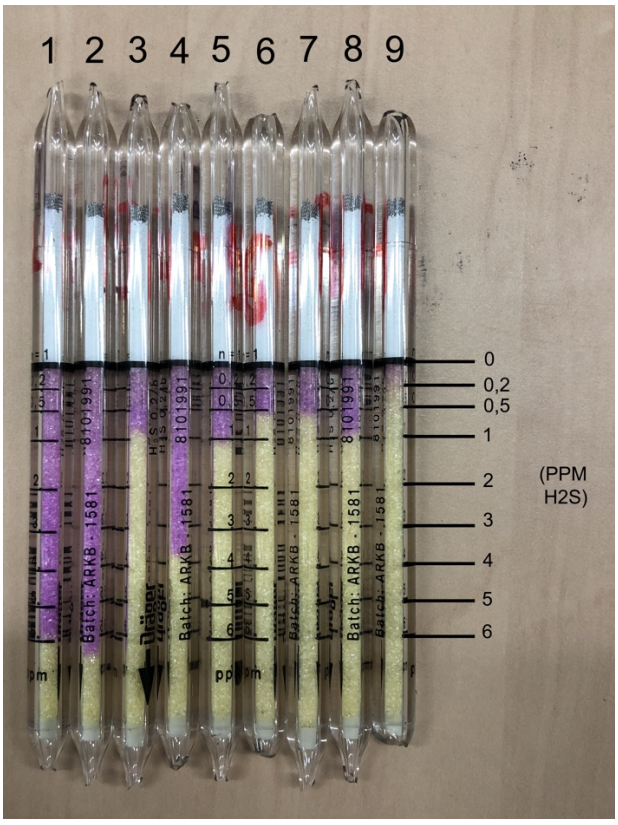


Figure 25 Dräger tubes measurement results.

Table 9 Overview of the Dräger tube measurements performed.

Feed H_2S	Dräger Tube	Test Objective	Measured H_2S
6 ppm	1	Control	6 ppm
	2	Control	6 ppm
	3	Isopropanol	1 ppm
	4	H_2SO_4/Isopropanol mixture	4 ppm
1 ppm	5	Control	1 ppm
	6	Isopropanol	0,5 ppm
	7	H_2O	0,5 ppm
	8	H_2SO_4/Isopropanol mixture	1 ppm
	9	N_2 + Isopropanol	0 ppm

The first measurement was a blank test to see if the prepared amount of sulphur in the gas bags was measured by the Dräger tube, and thus to check whether the hand pump could provide sufficient suction. It would be a strong indicator that the hand pump could provide sufficient suction if the value measured with the tube is the same as the actual

value prepared in the gas bag. Indeed, the first Dräger measurement read 6, 6 and 1 ppm resp. (tubes 1, 2 and 5 in figure 25). It took the hand pump longer to suck 100 mL but eventually it succeeded, proving that it can provide enough suction to suck gas from a line that is at 0.6 ATM and give a correct measurement.

The second test was to validate that isopropanol does indeed capture most (or all) of the sulphur from the gas that is bubbled. Dräger tubes 3 and 6 measured 1 and 0,5 ppm resp. after bubbling syngas with 6 and 1 ppm resp. through the isopropanol liquid. As expected, most of the sulphur was captured by the isopropanol. This effect causes the measurements done by Dräger tubes to be false (lower than actual values are read).

The proposed solution to stop the capture of sulphur by isopropanol was made by adding 30% H_2SO_4 to isopropanol in a 50:50 ratio. (Zeisler, 2010) The H_2SO_4/Isopropanol mixture was prepared by adding 25 mL of 30% H_2SO_4 (in water) to 25 mL of isopropanol. Dräger tubes 4 and 8 show the result of this test (figure 25). From the 6 ppm H_2S gas bag, the Dräger tube measured a value of 4 ppm H_2S, proving that the H_2SO_4 mixture helps in blocking isopropanol in capturing H_2S. From the 1 ppm H_2S gas bag, the Dräger tube measured a value of 1 ppm, none of the sulphur was captured by the H_2SO_4/isopropanol mixture.

An additional test was done to see if the sulphur captured by the isopropanol would stay in the liquid or would be released in gas phase if flushed with nitrogen. If the nitrogen carries the sulphur from the isopropanol mixture, it could cause harmful implications, such as wrong readings for following measurements or contaminating the line downstream with H_2S. The isopropanol that had captured some sulphur was flushed by nitrogen and the gas was measured with Dräger tube 9. The value measured was 0 ppm H_2S in N_2 gas from which can be concluded that the sulphur does not escape the isopropanol gas.

In conclusion, this side test has validated the following:

1. The Dräger Accuro hand pump used for Dräger tube measurements is capable of sucking gas from a line which is at under pressure. The pressure tested at was 0.6 ATM (pressure in the GCU is approx. 0.8 ATM) and the pump managed to suck the gas through, although taking longer for each stroke (up to 30 sec per stroke).
2. Mixing 30% H_2SO_4 with isopropanol helps to create a solution which removes the tars from the gas but does not capture sulphur in the process. The tests show that for the gas contaminated with H_2S almost all sulphur bubbles through the solution without being captured. In the case of 6 ppm H_2S in-line concentration the Dräger tube measured 4 ppm after adding H_2SO_4 compared to 1 ppm with only isopropanol. For the 1 ppm H_2S in-line concentration test the Dräger tube measured 1 ppm after adding H_2SO_4, compared to 0.5 ppm with only isopropanol.

3. Sulphur that is contained in the isopropanol solution will not leave the solution in gas-phase after flushing by nitrogen.

3.2 Sampling train

The sampling train is used to collect the main contaminants HCl, H_2S and tar samples through bubbling or gas bag collection which later can be analyzed for its main gas composition with Non-Dispersive Infrared Spectrometer (NDIR) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The sampling train has two inlets, one for either HCl and H_2S sampling and the other inlet for tar sampling (using an adapted Tar Protocol). Silica gel and Activated Carbon are used to avoid moisture and tar from entering the pump or NDIR.

Since the system is at below atmospheric pressure, a pump is needed to suck the gas through the sampling lines. To adjust the flowrate a needle valve and rotameter are placed in the line, together with a flow totalizer to measure the flow rates. Also, a thermocouple is placed to measure the temperature at the flow totalizer. A pressure gauge is also installed in the line to (1) perform a leak test and (2) monitor the suction pressure in the line for gas volume calculations.

A Piping and Instrumentation Diagram (P&ID) of the sampling train can be found below in figure 26 and a photo of the actual setup in figure 27 (the P&ID of the whole integrated system including gasifier, GCU and SOFC can be found in Appendix A).

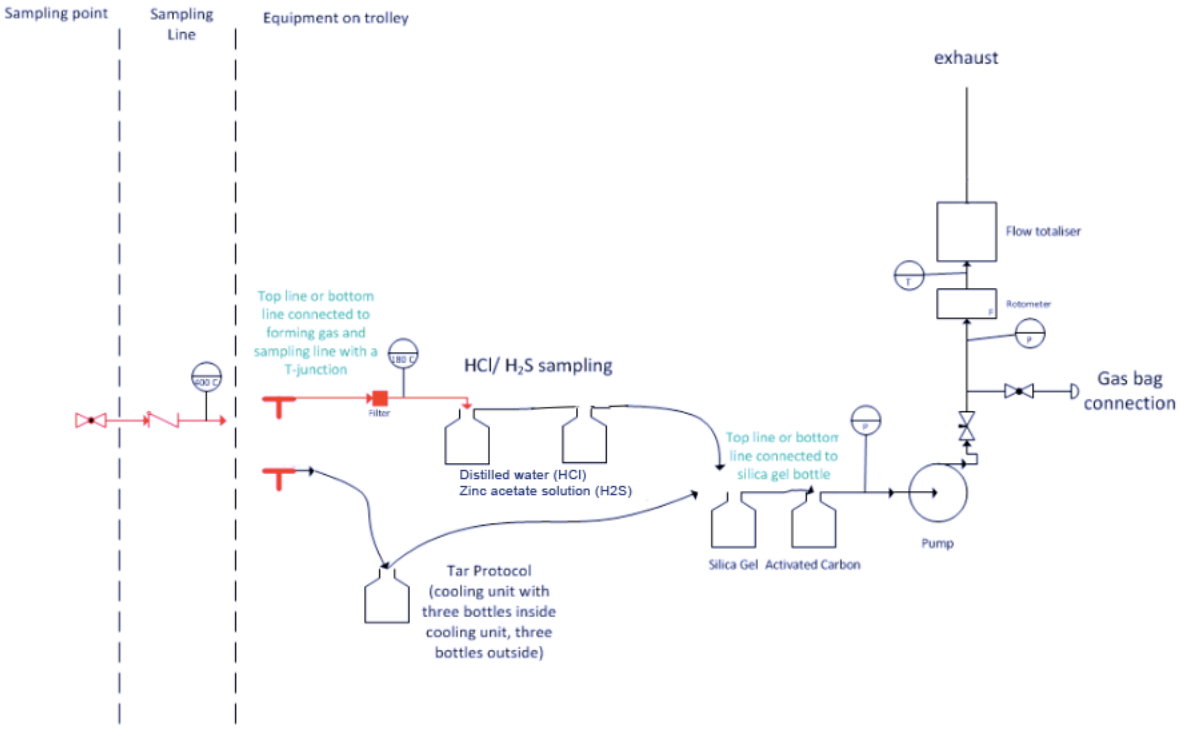


Figure 26 P&ID of the sampling train for sampling HCl, H2S and tar compounds.

Figure 27 Lower level of the sampling train setup. Shown are the activated carbon filter, the silica gel, pressure gauge, flow totalizer and exhaust line

3.3 HCl and H_2S sampling procedure

In this section, the procedure for HCl and H_2S sampling is described in steps. The description of the equipment is given in Chapter 3.6.

1. The tar filter is heated to 125 °C.
2. The heaters for the sampling lines are turned on at 400 °C.
3. Place the two impinger bottles containing 30 ml distilled water (for HCl measurement) or 30 ml 5% zinc acetate solution (for H_2S measurement) in between the tar filter and the silica gel containing bottle.
4. The initial values for flow totalizer, temperatures and pressures are recorded.
5. The pump is started and the timer is set. The desired flow rate (0.12 Nm_3/h) can be set by adjusting the rotameter and the needle valve accordingly.
6. The gas bubbles through the bottles for the desired/calculated sampling time.
7. After the sampling time is passed, first the ball valve is closed and right after the pump is turned off.
8. The end values for the flow totalizer, temperatures and pressures are immediately recorded.
9. The two bottles are poured in to two different sampling bottles (end volumes are recorded) and are stored in a refrigerator until transported to TU Delft for analysis. No rinsing fluid is used for the HCl measurements. For H_2S, the liquid that remains on the sides of the impinger bottle is rinsed with distilled water and added to the sampling bottle (note the volume before and after adding the rinsing fluid).

Figure 28 below shows the HCl bubbling equipment.

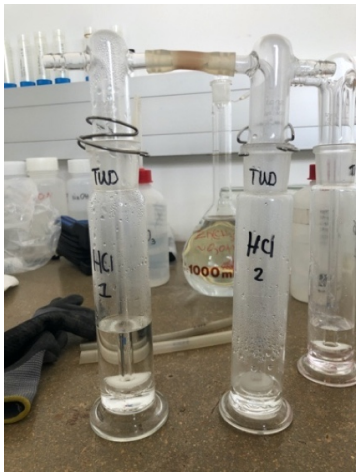


Figure 28 Two impinger bottles connected via a rubber tube to collect HCl samples with.

3.4 HCl and H_2S analysis

The method used to analyze the stored solutions with HCl and H_2S is the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES). The detection limit of this method is 0.1 ppm for HCl and 0.5 ppm for H_2S. The content analysis is done at TU Delft.

3.5 Tar sampling procedure

In order to sample the tar, the gas is run through bottles with isopropanol that captures the tar compounds. The train consist of four bottles containing 50 mL isopropanol. The first bottle acts as a moisture collector and will be placed outside the cooling bath at room temperature to prevent freezing of the condensed water. The second, third and fourth bottle will be filled with 50 ml of isopropanol and their temperature will be held at approx. -20 °C. Additionally, an empty bottle (at temperatures of around -20 °C) is put at the end of the line to collect volatile compounds that may have not been captured by the previous bottles. There must also be a particulate filter before the bottle train, as these particulates can sabotage measurements and damage the pump. The pump and volume flow meter are placed after the line to produce and measure the flow. The solutions in the bottles are collected and analyzed with GCMS (Gas Chromatography Mass Spectroscopy) and Gravimetric analysis.

Below, in figure 31, an example of a tar sampling line is shown schematically. To improve surface area of the gas with the isopropanol, glass frits are placed in the second, third and fourth impinger bottles (the bottles which are placed in a cooling bath of -20 °C).

The contents of all impinger bottles are added in to a bottle to be stored for analysis. To also capture the tar that remains inside the pipe and on the walls of the bottle, acetone is used to flush the bottles. The acetone solution with the flushed tar must be measured before mixing with the isopropanol solution.

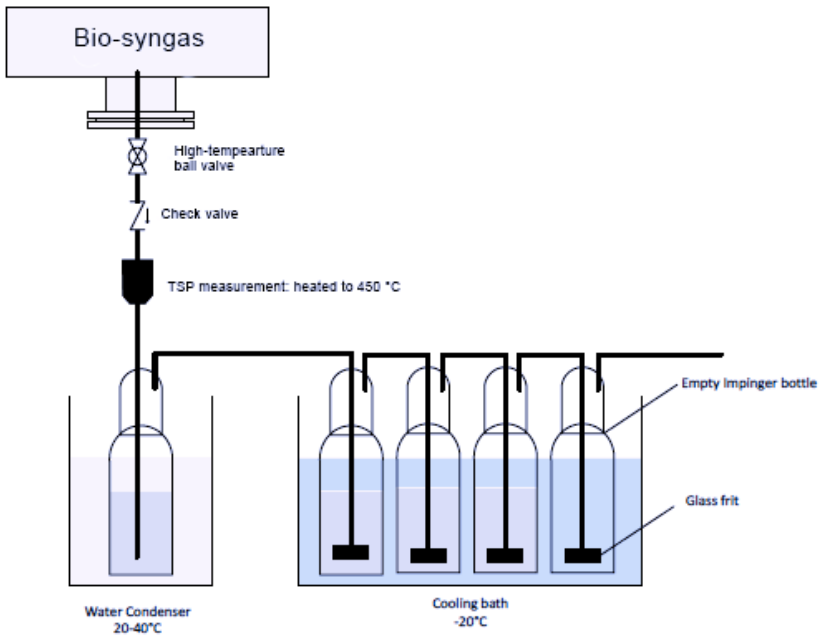


Figure 29 Schematic overview of tar sampling with isopropanol solutions.

3.6 Tar Analysis

The stored tar must then be analyzed to determine the amount of tar in the gas. Several methods to analyze tar compounds exist, depending on the operation conditions of the system and what information is required. (Van de Kamp, 2005) Here, two methods of tar analysis are used: 1) Gravimetric analysis and 2) Gas Chromatography-Mass Spectroscopy (GCMS) analysis.

1. *Gravimetric*: with this method, the residue of tar is weighed which is obtained by evaporating the isopropanol solution containing tar and will result in a general mg/l of solvent concentration. With this method, lighter tar compounds are generally not measured due to evaporation.
2. *GCMS*: with this method, compounds that are smaller than coronene can be measured, and each individual (light) tar compound can be distinguished and analyzed separately.

Tar analysis will be performed by ECN/TNO. The samples will be analyzed based on two protocols to capture most of the tar compounds.

3.7 Sampling train parts list

The parts required for the sampling train shown above can be found in the table below.

Table 10 Parts list for the sampling train used for measurements in Graz (BIOS).

Item	Description/Comment
High temp. ball valve	
Check valve	To prevent flow in reverse direction
T-junction	Male T-connection
Filter in HCl/H2S line	To remove tar in HCl and H2S sampling
Thermocouple in HCl/H2S line	To maintain filter temperature at 150-180 °C.
3x Impinger bottle	Contains distilled water for HCl sampling
3x Impinger bottle	Contains NaOH for H2S sampling
3x Impinger bottle	For cooling bath in tar sampling
3x Impinger bottle	For outside cooling bath in tar sampling
3x Impinger bottle	Extra bottles
1x Cylinder 200 mL	Extra
1x Erlenmeyer 500 mL	Extra
Vessel	To hold Silica Gel
Silica Gel	To remove moisture
Vessel containing activated carbon	To remove tar compounds
Pump	To suck gas through sampling lines to exhaust or gas bag or NDIR lines.
Needle valve	To shut down gas after pump.
Ball valve	To shut down gas going to the gas bag line.
Flow totalizer	To measure total flow
Rotameter	To measure/adjust flow rate
Temperature controllers	To set temperature
Thermocouples	To measure temperature
1x pressure gauges	To measure pressure at different points.
12x Impinger bottle heads	
+/- 7 m Stainless steel lines	6 mm line
Trace heaters	5x 4m lines (450 °C) 4x 2m lines (450 °C) 2x 2m lines (250 °C)
Ferrule set	
6 mm male to male connections	10 pieces
6 mm T-junctions	6 pieces
6 mm three-way valve	6 pieces
6 mm check valves	6 pieces

3.8 System design

The Combined Heat and Power (CHP) system consists an integrated updraft gasifier (50 kW nominal fuel power) with a SOFC and is designed to convert flexible biomass fuels into heat and power. Part of the formed gas in the gasifier (raw syngas) is combusted in an afterburner and its thermal energy is collected through a water boiler. The other part (12 kW_{th}) of the raw syngas is fed to a SOFC system (6 kW_{el}) to produce electrical energy. In between the gasifier and SOFC a Gas Cleaning Unit (GCU) is integrated, which purifies the raw syngas from the contaminants which cause damage to downstream equipment/systems.

The figure below (figure 32) shows the design temperatures for the complete process.

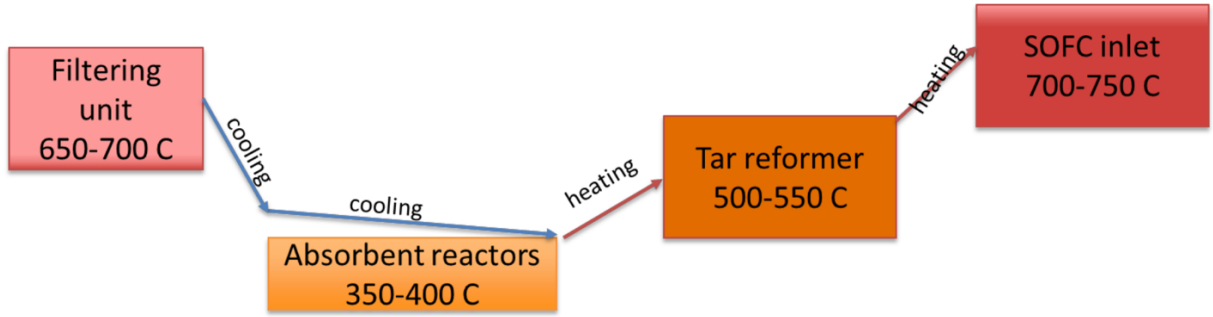


Figure 30 Design temperatures for the optimized GCU (GCU2). (Chundru, 2017)

The unit filter used are ceramic candle filters. A K_2CO_3 based absorbent material ('HTG-1' from manufacturer Haldor Topsoe) is used in the HCl removal stage. For the H_2S removal stage a ZnO based absorbent material with an ZnO/CuO based guard layer is used. The tar reactor is a catalytic packed bed reformer.

3.9 Chapter summary

In this chapter the methodology of the experiments is explained. Both H_2S and HCl are sampled via two methods: gas bubbling and Dräger tubes. In gas bubbling, different absorbing liquids are used. For HCl the absorbing liquid is water, while a Zinc Acetate solution is used for H_2S. Dräger tubes are used for direct on-site measurement of HCl and H_2S concentration. A side-test was performed at TUD in which the tubes were tested for under pressure performance and the effect of H_2SO_4 on the measurements. The tar sampling is done by BIOS.

Both the HCl and H_2S samples will be measured by ICP-OES at TUD. The analysis of the tar samples is done by ECN/TNO.

4 Results and Discussion

4.1 Temperature evaluation

The required temperatures (350 °C) for both the HCl and H2S reactors was met and kept steadily throughout the test runs. Gasifier temperatures were almost always over 800 °C, which indicates a normal gasification process taking place. Keeping the tar reformer at steady temperatures gave the most difficulties during operation. Ideally the tar reformer should be at least 500 °C, and preferably higher, but during the test runs many times this temperature would drop to around 475 °C. This decrease in temperature most likely occurred due to a heat leak caused by a defect pipe section (figure 33 below). This pipe section lies between the afterburner and the tar reformer where the heat of exhaust gas is recuperated to heat up the tar reformer. The temperature of the pipe containing the exhaust gas dropped from approx. 550 °C to 400 °C.

Figure 31 Defect pipe section between tar reformer and afterburner stripped down and checked for leaks. This was causing the tar reformer to not be able to reach its operating temperature and eventually delayed the test runs.

4.2 HCl and H_2S results

Syngas was sampled using a sampling train connected to the gasifier-GCU-fuel cell setup at BIOS. In total 32 HCl samples were taken. The samples were taken from the four sampling points: downstream gasifier, downstream HCl reactor, downstream H2S reactor and downstream tar reformer. For each sampling point, measurements were done twice and on two different test days (4 sampling points x 2 measurements each x 2 test days = 16 samples for each contaminant). The measured variables include the volume

before/after bubbling, flowrate, pressure and temperatures at each of the sampling points as well as at the gasifier, tar reactor, tar filter and sampling train exhaust.

The 32 samples were sent back to TU Delft where our lab chemist analyzed them for Cl and S contents via ICP-OES analysis. The results showed that in almost all samples, except for one, the concentrations S and Cl were 0 ppm.

These results could be explained by three possible reasons:

1) The syngas samples contain no sulphur or chlorine. Since we know the wood chips fuel produces syngas which does contains sulphur and chlorine, this would imply that the GCU has performed very well and that it purified the gas from all sulphur and chlorine contents. This however seems unlikely, as the samples at the first sampling point, which is the point upstream the GCU, should then have HCl and H_2S content. This implies the problem has to do with correct sampling and/or analysis. Unfortunately cross-checking the results with BIOS' results was not possible, which could confirm or deny this proposition.
2) The sulphur and chlorine concentrations could not be detected because the detection limit of the ICP-OES. This limit is 0.5 ppm and it means that any concentration detected by that ICP-OES that is smaller than 0.5 ppm would result in a 0 ppm measurement.
3) Another method of analysis should have been used. To solve this issue, the H_2S samples must be analyzed through photometry analysis methods. However, this does not explain the results for chlorine, as HCl is very soluble in water and should be detected by the ICP-OES. This also implies the sampling procedure was not robust.

4.3 Tar results

Samples were taken from two sampling points before and after the GCU, i.e. upstream and downstream GCU resp., on two different test days. In total, four liquid tar samples were sent to ECN to analyze for the different tar components (see figure 34). Table 11 below shows the description and relevant data for each sample.

Table 11 Description of the four tar samples.

Tar sample nr.	Sample date	Sampling point
1	30.01.19	Upstream GCU
2	30.01.19	Downstream GCU
3	31.01.19	Upstream GCU
4	31.01.19	Downstream GCU

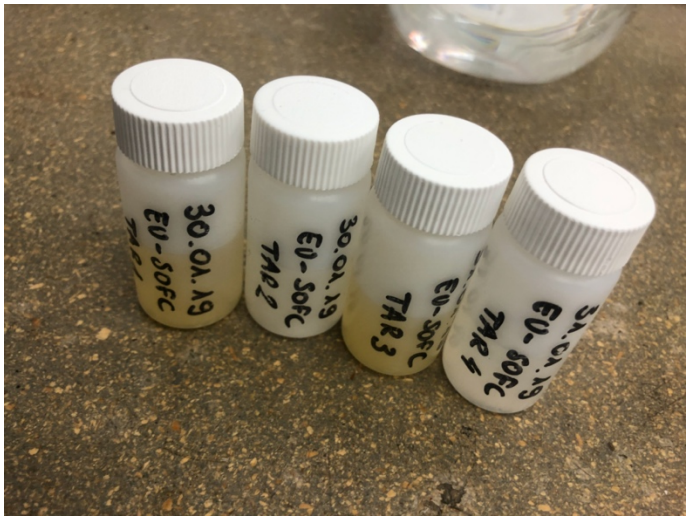


Figure 32 Tar samples taken upstream and downstream the GCU. The colors of the liquids indicate lower tar components after the GCU.

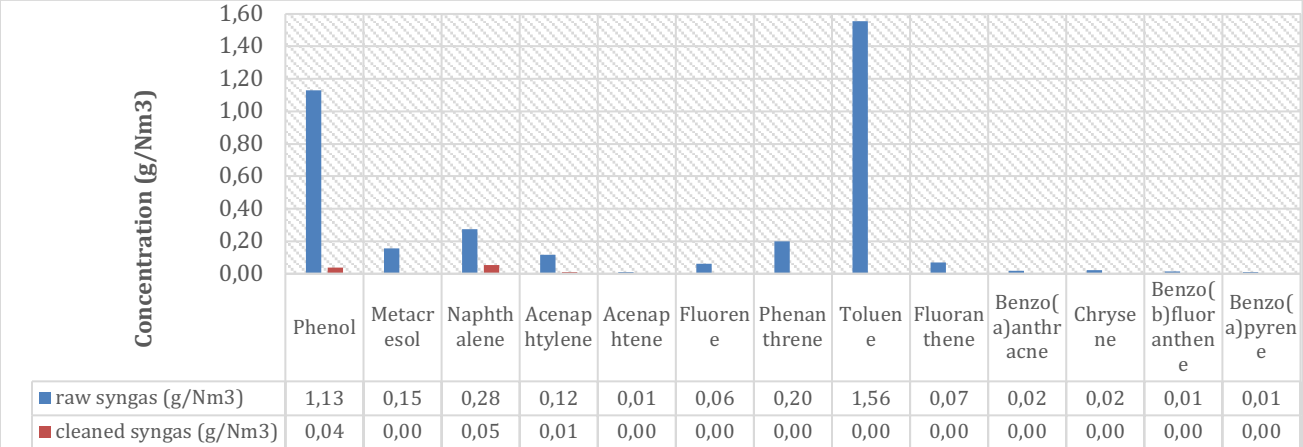
To include most tar components, the samples were analyzed according to two different tar analysis protocols. These protocols are B.C302 ('determination of pyrolysis bonds') and B.C303 ('determination of polycyclic aromatic hydrocarbons'). Table 12 shows the tar components that are found in the syngas derived from wood chips, while a comprehensive tar component list can be found in appendix B.

Table 12 Tar component analysis of the tar samples

Substance group	Tar Component	Chemical formula	Molar mass (g/mol)	Boiling point °C
Heterocyclics	Phenol	C_6H_6O	94	181.7
	Metacresol	C_7H_8O	108.14	203
Light Polycyclic Aromatic Hydrocarbons	Naphthalene	$C_{10}H_8$	128.0	21
	Acenaphtylene	$C_{12}H_8$	152.19	280
	Acenaphtene	$C_{12}H_{10}$	154.2	279
	Fluorene	$C_{13}H_{10}$	166.2	295
	Phenanthrene	$C_{14}H_{10}$	178.23	340
	Toluene	C_7H_8	92.14	110.6
Heavy Polycyclic Aromatic Hydrocarbons	Fluoranthene	$C_{16}H_{10}$	202.26	375
	Benzo(a)anthracne	$C_{18}H_{12}$	228.29	438
	Chrysene	$C_{18}H_{12}$	228.09	448
	Benzo(b)fluoranthene	$C_{20}H_{12}$	252.2	481
	Benzo(a)pyrene	$C_{20}H_{12}$	252.31	495

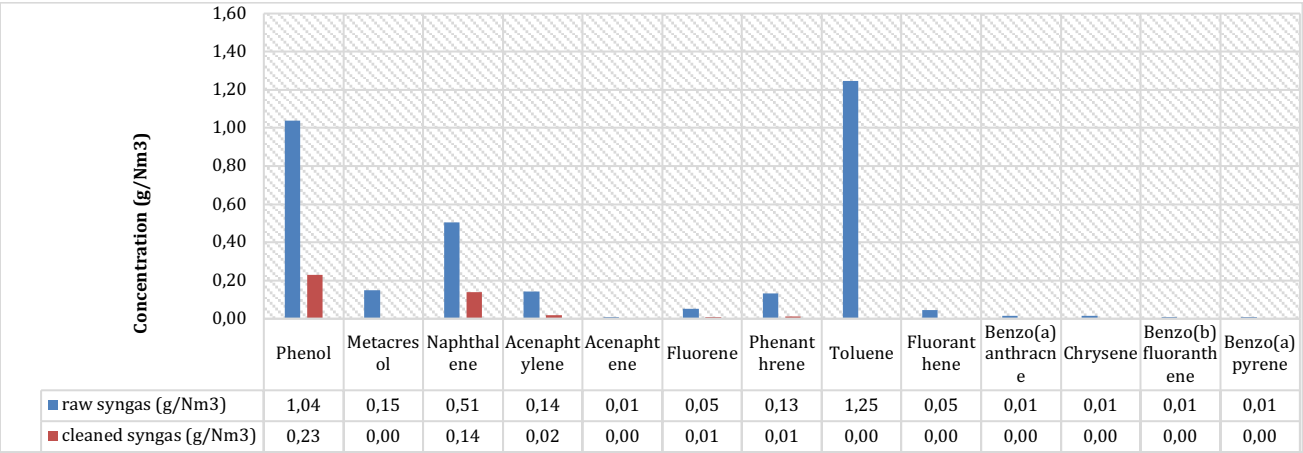
Of the measured quantities of tar components in the syngas, approx. 15% are heterocyclic compounds, 38% are light PAHs and 46% are heavy PAHs.

Since the results are in mg tar component per kg tar sample, they need to be converted to grams of tar component per Nm^3 of syngas to be able to compare the results. This is done by taking into account the sampling time, the solution data, and the dry sample weight. The concentration of the specific tar components of the first and second test day can be found in figure 35 and 36 respectively.



	Phenol	Metacresol	Naphthalene	Acenaphtylene	Acenaphtene	Fluorene	Phenanthrene	Toluene	Fluoranthene	Benzo(a)anthracne	Chrysene	Benzo(b)fluoranthene	Benzo(a)pyrene
raw syngas (g/Nm3)	1,13	0,15	0,28	0,12	0,01	0,06	0,20	1,56	0,07	0,02	0,02	0,01	0,01
cleaned syngas (g/Nm3)	0,04	0,00	0,05	0,01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00

Figure 33 Concentrations of the specific tar components before and after gas cleaning on the 1st test run (30-01-19).



	Phenol	Metacresol	Naphthalene	Acenaphtylene	Acenaphtene	Fluorene	Phenanthrene	Toluene	Fluoranthene	Benzo(a)anthracne	Chrysene	Benzo(b)fluoranthene	Benzo(a)pyrene
raw syngas (g/Nm3)	1,04	0,15	0,51	0,14	0,01	0,05	0,13	1,25	0,05	0,01	0,01	0,01	0,01
cleaned syngas (g/Nm3)	0,23	0,00	0,14	0,02	0,00	0,01	0,01	0,00	0,00	0,00	0,00	0,00	0,00

Figure 34 Concentrations of the specific tar components before and after gas cleaning on the 2nd test run (31-01-19).

Toluene (40%), phenol (31%) and naphthalene (9%) together make up the biggest fraction of the tar components, adding up to a combined 80% of the tar components. Researchers often use these compounds as model tars for simulated experiments. The different tar compounds should not be generalized, as some compounds can be reformed and function as fuel, while other tar compounds act as poison, even in small quantities. In a recent study it was found that toluene and benzene could be reformed internally and

that naphthalene acted as a poison. (Cavalli A. & Aravind P.V., 2019) Figure 37 shows the total tar concentrations (g/Nm^3) in the syngas on both test days.

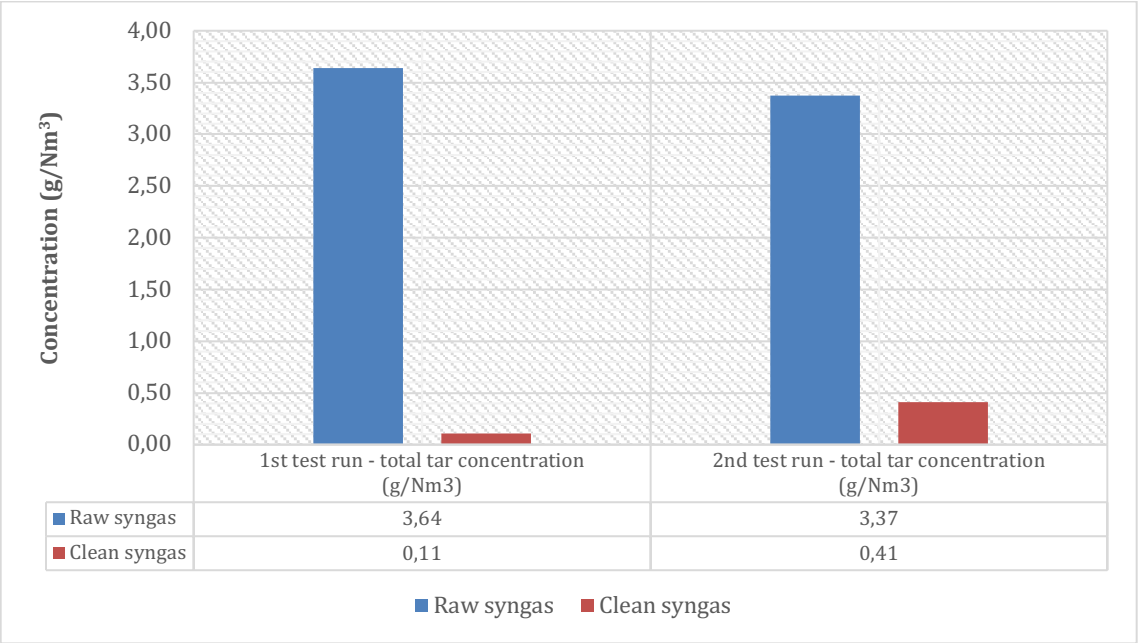


Figure 35 Total amount of tar in the syngas stream before and after cleaning.

4.3 Dräger tube Results

Dräger tubes were used as an extra method of measuring HCl and H_2S in the syngas. They are useful since they are easy to use and can provide quick on-site measurements. The syngas was analyzed for HCl and H_2S concentration at different sampling points (before and after GCU and in between the reactors). However, the Dräger tubes could not determine the concentration of HCl or H_2S in the syngas. Figure 38 shows the Dräger tubes used to measure HCl in the syngas.

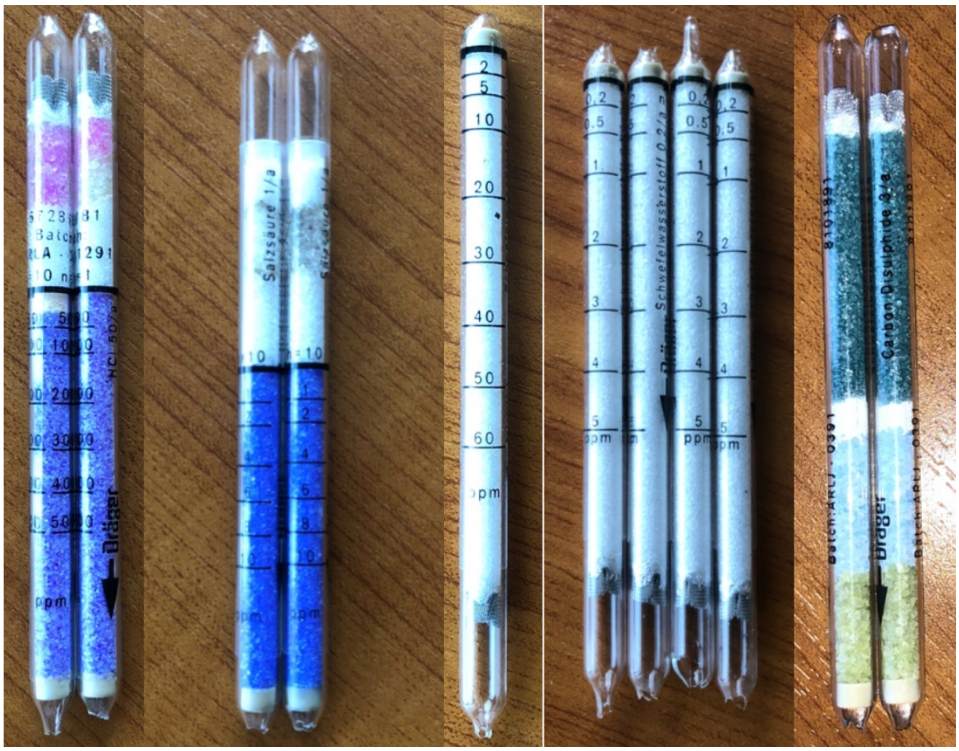


Figure 36 HCl and H_2S Dräger tubes. From left to right: 2x HCl 500-5000 ppm, 2x HCl 1-10 ppm, 1x HCl 2-60 ppm, 4x H2S 0.2-5 ppm, 2x C2S 3-95 ppm.

It can be seen that in the pre-layer (top section), the white reacting material changed color to pink (left tubes, range 500-5000 ppm) and grey/clear (right tubes, range 1-10 ppm) resp. The pre-layer has three purposes: 1) to adsorb moisture, 2) to trap interfering substances and to 3) convert substances to measurable substances. (Dräger, 2020) In normal measuring conditions this pre-layer should not change in color. When taking the measurements, the pump had difficulties sucking the gas through the tube. In the side-test performed at TU Delft with pure H_2S the pump was able to suck the gas through the pump at 0.8 ATM. This indicates that another factor caused the pressure drop which made the suction of the pump be insufficient to suck gas through the tube.

A possible explanation for these results is a cross-influence of the many compounds in the syngas with the Dräger tube reactive material. These compounds could be reacting with the reactive material and clog up the tube, preventing the gas to go through the indication layer. Another possible explanation is that the syngas has a higher moisture content and a higher temperature than the Dräger tube condition range. These effects were not taken into account as in the side-test simulated gases were used and not real syngas, and were at room temperature without any moisture content.

4.4 Discussion

Temperature evaluation

Keeping the temperatures steady throughout the process is an important factor that can greatly influence the syngas composition, gas cleaning effectiveness and the electrical output. The effect of temperature on tar reforming has been studied extensively in the literature and it is found that at lower operating temperatures inside the tar reformer generally less tar is reformed. The first stage GCU (GCU1) experienced high heating losses, which were addressed in the improved GCU (GCU2) by adding electrical trace heaters, removing large valves which act as heat sinks and by using fewer mechanical connections. These modifications helped in keeping temperatures levels steady and reducing heat losses. However, it is these modifications which cause the system to be less reliable and more costly (compared to cold gas cleaning).

Tar Results

Tar results were obtained on two different test runs in which woody biomass was used as the fuel. The total tar concentration on the 1st and 2nd test runs were reduced by 97% and 88% resp. The cleaned syngas in the two test runs has a total tar concentration of 0.11 g/Nm^3 (≈ 0.02 ppmv) and 0.41 g/Nm^3 resp. (≈ 0.08 ppmv), which is well below the threshold of 1 ppmv. The higher tar concentration in the syngas in the 1st test run compared to the 2nd test run is most likely caused due to the non-uniformity of the woody fuel and the slightly different operating temperatures in the reactors. The variation in the operating temperature affects the tar degradation (as can be seen in figure 10), which can cause deviations in the specific tar compounds. The results indicate higher concentration of toluene, phenol and naphthalene compared to the other tar compounds. It is found that toluene and benzene be internally reformed inside the SOFC and thus act as a fuel, while other compounds, such as naphthalene, act as a poison. (Cavalli A. & Aravind P.V., 2019) However, extensive research on this topic is still needed to fully understand the dynamics of specific tar compounds in a SOFC.

HCl and H_2S results

The key learning points from the HCl and H_2S measurements are related to proper sampling and analysis. HCl and H_2S sampling could have been improved by performing leak test at different moments during the test runs to ensure that there is no failure in any of the components. During the first trip a broken glass connection was discovered underneath the isolation tape, which caused a leak. After replacing this part, the samples turned yellowish and became warmer to the touch, indicating that now the syngas was passing through the liquids correctly. Furthermore, the samples were stored at 5 to 10 °C before being transported back to the Netherlands, which may have affected the solution. Other learning points are with regards to the analysis.

The HCl and H_2S samples were analyzed via ICP-OES, which can measure ions in aqueous solutions. It is possible that the tar filter on the sampling train did not (fully) capture all the tar compounds and contaminated the samples. However, it was not an option to perform tests on the sampling train to ensure its effectiveness because of limitations due to the sampling train being in Graz and being dependent on a strict schedule for the test runs.

Dräger tubes results

According to Dräger, although the tubes are tested for certain operating conditions, they are also capable of accurate determination at much lower or higher humidification levels. However, this is not the case for deviating temperatures. At very high or low temperatures the reaction some reagents may resp. evaporate or freeze. Also, the rated temperature of the Dräger tubes is between 5 to 40 °C. Since the Dräger tube is inserted in-line directly after the H_2SO_4/Isopropanol solution, its temperature may very well have been higher than 40 °C. The gas in sampling line is at 400 °C and cools down rapidly as it enters the sampling train. The bubbling through the H_2SO_4/Isopropanol solution furthermore cools down the syngas. However, despite the cooling, the syngas may have been still too hot for measurement with the Dräger tube. Another effect this can cause, alongside freezing or evaporation of the reagents, is that the gas expands at higher temperatures, resulting in a higher volume for which the Dräger tube is not calibrated.

5 Conclusions

The objective of this experimental research was to measure if the Gas Cleaning Unit, in a gasifier-GCU-SOFC integrated system built by TU Delft and HYgear, was able to meet the requirements in terms of effectively removing contaminants from bio-syngas. Biomass derived syngas contains impurities which can cause damage to downstream equipment. The cleaning of the gas from these contaminants has been investigated in this report. To do this, HCl, H_2S and tar samples have been collected and analyzed. For HCl and H_2S two methods of analysis were used: ICP-OES and Dräger tubes. Tar was collected and analyzed by ECN/TNO following the tar protocols and measured by GC-MS.

HCl and H_2S samples collected from gas bubbling and Dräger tubes gave incorrect results (0 ppm), probably caused by 1) faulty sampling/sampling train, 2) low values/below detection limit or 3) method of analysis. Extended research should be focused on sampling and analysis of real gas and the effect of cross-influence of the different syngas compounds. Further testing should be done with Dräger tubes in CHP systems as they can provide easy and quick on-site measurements. These tests should be performed with real syngas and at different gas temperatures and moisture contents, as opposed to simulated gas in a lab.

Tar samples were collected before and after the gas cleaning stage. Analysis of the samples show 3.64 g/Nm^3 (1st test run) and 3.47 g/Nm^3 (2nd test run) of total tar concentration and 0.11 g/Nm^3 and 0.41 g/Nm^3 resp. after gas cleaning. This is a reduction of 97% and 88% respectively. The cleaned syngas had 0.02 ppmv and 0.08 ppmv of total tar concentration, which is well below the threshold of 1 ppmv for SOFC operation.

The tar components consisted of approx. 15% heterocyclic compounds, 38% light PAHs and 46% heavy PAHs. Naphthalene, toluene and phenol comprised of over 81% of the total tar concentration.

The temperature evaluation shows a normal heating up of the gasifier and reactors during the test runs. The design temperature parameters were achieved.

High temperature gas cleaning of bio-syngas has great potential to effectively reduce HCl, H_2S, tars and particulate matter to such low levels that they do not harm the fuel cell. It is found that the GCU2 has improved results over the GCU1, largely due to less heating losses which in term resulted in a more effective cleaning. Further research should be directed towards the cross influence of the different tar compounds and the contaminants that are found in bio-syngas.

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Appendices

Appendix A – System overview

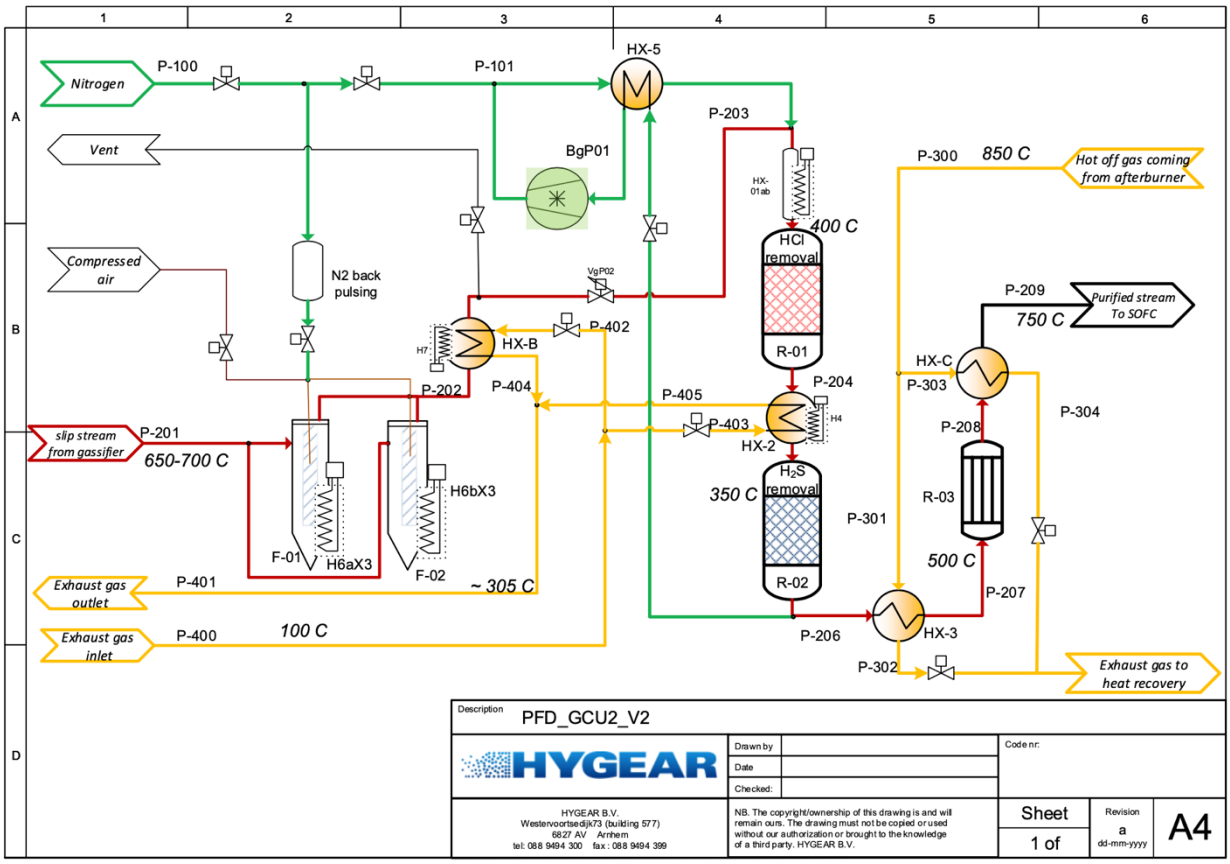

Figure 37 P&ID of integrated system consisting of a gasifier, GCU and SOFC stack.

Appendix B – Tar results for upstream and downstream GCU measurements – full tar compound list.

The analysis with B.C302 protocol measured mg/kg of the following tar components (table 13):

Table 13 Tar analysis with tar analysis protocol B.C302.

Tar Compound	Tar Concentration (g/Nm^3)			
Acetaldehyde	46.2	<10	48.8	<10
Methylformate	<5	<5	<5	<5
Propanal	<10	<10	<10	<10
Furan	<5	<5	<5	<5
Isobutyraldehyde	<10	<10	<10	<10
Aceton	nd	nd	nd	nd
Methylacetate	<10	<10	<10	<10
Methanol	105.5	27.6	92.1	32.3
Toluene	52.2	<5	78.0	<5
o-Xylene	<5	<5	<5	<5
Hydroxyaceton	<5	<5	<5	<5
Hydroxyacetaldehyde	<10	<10	<10	<10
1-Hydroxy-2-butanone	<10	<10	<10	<10
Angelicalactone	<5	<5	<5	<5
Acetic acid	11	<10	<10	<10
2-Furaldehyde	<5	<5	<5	<5
Formic acid	<10	<10	<10	<10
5-Methyl-2-furaldehyde	<5	<5	<5	<5
Coumaran	<5	<5	<5	<5
2-Furanmethanol	<5	<5	<5	<5
Naphthalene	nd	nd	nd	nd
2(5H)-Furanone	<5	<5	<5	<5
2-Methoxyphenol	<5	<5	<5	<5
4-Methylguaiacol	<5	<5	<5	<5
o-Cresol	<5	<5	<5	<5
Phenol	37.9	10.7	65	16
4-Ethylguaiacol	<5	<5	<5	<5
p-Cresol	<5	<5	<5	<5
m-Cresol	5.2	<5	9.4	<5

2-methoxy-4-propyl-phenol	<5	<5	<5	<5
Eugenol	<5	<5	<5	<5
4-Ethylphenol	<5	<5	<5	<5
2-methoxy-4-vinyl-phenol	<5	<5	8.9	<5
4-Propylphenol	<5	<5	<5	<5
2.6-Dimethoxyphenol	<5	<5	<5	<5
Levulinic acid	<10	<10	<10	<10
Isoeugenol	<5	<5	<5	<5
4-Methylsyringol	<5	<5	<5	<5
5-(Hydroxymethyl)-2-furaldehyde	<5	<5	<5	<5
3-Methoxypyrocatechol	<10	<10	<10	<10
4-(2-propenyl)syringone	<5	<5	<5	<5
Vanilline	<5	<5	<5	<5
Acetovanillone	<5	<5	<5	<5
Pyrocatechol	<5	<5	<5	<5
Phenanthrene	nd	nd	nd	nd
Syringaldehyde	<5	<5	<5	<5
4-hydroxybenzaldehyde	<5	<5	<5	<5
2-Methoxyhydroquinone	<20	<20	<20	<20
4-Hydroxybenzylalcohol	<5	<5	<5	<5
Acetosyringone	<5	<5	<5	<5
4-Hydroxyacetophenone	<5	<5	<5	<5
Hydroquinone	<5	<5	<5	<5
Resorcinol	<5	<5	<5	<5
Coniferylalcohol	<10	<10	<10	<10
Pyrene	nd	nd	nd	nd
Levoglucosan	<10	<10	<10	<10
2.6-dihydroxy-4-methoxyacetophenone	<10	<10	<10	<10

Appendix B (Continued)

The analysis with B.C303 protocol measured mg/kg of the following tar components (table 14):

Table 14 Tar analysis with tar analysis protocol B.C303.

Tar Component	Tar concentration (g/Nm3)			
	30-1-19 upstream GCU	30-1-19 downstream GCU	31-1-19 upstream GCU	30-1-19 downstream GCU
Naphthalene	9.26	15.12	31.62	9.64
Acenaphtylene	3.93	3.31	8.94	1.29
Acenaphtene	0.3	<0.25	0.64	<0.25
Fluorene	2.03	0.85	3.2	0.5
Phenanthrene	6.73	1.14	8.38	0.8
Anthracene	1.63	<0.25	2	<0.25
Fluoranthene	2.39	<0.25	2,92	<0.25
Pyrene	2.02	<0.25	2,58	<0.25
Benzo(a)anthracene	0.65	<0.25	0,87	<0.25
Chrysene	0.68	<0.25	0,93	<0.25
Benzo(b)fluoranthene	0.47	<0.25	0,61	<0.25
Benzo(k)fluoranthene	<0.25	<0.25	<0.25	<0.25
Benzo(a)pyrene	0.36	<0.25	0,45	<0.25
Indeno(123-cd)pyrene	<025	<0.25	<0.25	<0.25
Dibenz(ah)anthracene	<0.25	<0.25	<0.25	<0.25
Benzo(ghi)perylene	<0.25	<0.25	<0.25	<0.25