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Master Thesis

Evaluation of gas impurity reduction of different feedstocks over the gas cleaning process of a 1 MW demonstration-scale dual fluidized bed gasification plant

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Kurzfassung

Um dem steigenden Interesse an Treibstoffen aus Biomasse und abfallbasierten Brennstoffen nachzukommen, wurde das bereits etablierte Prozesssystem der Dampf-Gaserzeugung mittels des Zweibettwirbelschichtverfahrens (DFB) an der TU Wien weiterentwickelt. Im Jahr 2022 wurde die neue Generation der Technologie mit adaptiertem Reaktordesign in einer 1 MW Demonstrationsanlage am Forschungsstandort (Syngas Platform Vienna) der Firma BEST Bioenergy and Sustainable Technologies GmbH das erste Mal in diesem Maßstab demonstriert. Die Abscheidung von im Gas vorhandenen Verunreinigungen passiert bis zu einem gewissen Grad in einem an den Gaserzeugungsreaktor anschließenden neuen konzipierten Gasreinigungssystem bestehend aus Strahlungskühler, Zyklon, Heißgasfilter, Wasserquench und RME-Wäsche. Seit der Inbetriebnahme wurden bereits fünf Versuchskampagnen mit unterschiedlichen Brennstoffen und verschiedenen Probenahmen und Messungen durchgeführt. Im Zuge dieser Masterarbeit wurden die Versuche an der Anlage praktisch begleitet und die Analysenergebnisse der Gasreinigung der ersten vier Versuchskampagnen hinsichtlich Wasser-, Partikel-, Teer-, Ammoniak und Schwefelwasserstoffgehalt ausgewertet. Ein Vergleich der Ergebnisse für unterschiedliche Brennstoffe über die einzelnen Reinigungsstufen wurde durchgeführt. Darüber hinaus wurde die aktuelle Datenlage mit bereits publizierten Ergebnissen aus Anlagen, welche das konventionelle Reaktordesign verwenden, verglichen. Die Resultate zeigen eine vergleichbare oder verbesserte Abscheidung von Verunreinigungen der neuen gegenüber der bisher etablierten Gasreinigung.

Abstract

In order to meet the increasing interest in fuels from biomass and waste-based fuels, the already established process system of steam gasification using the dual-bed fluidized bed (DFB) process was further developed at TU Wien. In 2022, the improved technology using an adapted reactor design was demonstrated for the first time in a scaled-up 1 MW demonstration plant at the research site (Syngas Platform Vienna) of BEST Bioenergy and Sustainable Technologies GmbH. The separation of impurities present in the product gas takes place - up to a certain level - in a newly designed gas cleaning system connected to the gasification reactor, consisting of a radiant cooler, cyclone, hot gas filter, water quench and RME scrubber. Since commissioning, five experimental campaigns have already been carried out with different fuels and various sampling and measurements. In the course of this master's thesis, the tests at the plant were practically accompanied and the analysis results of the gas cleaning of the first four experimental campaigns were evaluated with regard to water, particle, tar, ammonia and hydrogen sulfide content. A comparison of the results for different fuels across the cleaning stages was undertaken and compared with data from plants using the conventional reactor design of the DFB system. The results show a comparable or improved separation of impurities in the new system compared to the previously used system.

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1 Introduction

One of the greatest challenges facing mankind today is climate change. Phenomena like the raise of the global surface temperature or the raising concentrations of greenhouse gases (GHGs) over the past centuries can be illustrated by comparing the data records of the past decades, see Figure 1 and Figure 2 [1]. The data in Figure 1 shows an increase of the global surface temperatures which is a direct consequence of the incineration of fossil fuels such as coal, oil and natural gas. Figure 2 shows the increase of the CO₂ concentration as well as the CH₄ and NO_x concentrations in the atmosphere. The greenhouse gases originate from the burning of fossil fuels, therefore a direct correlation between these two values is generally assumed. As a result, global efforts have been initiated to reduce GHGs with a strong emphasis on the reduction of CO₂.

International agreements such as the Kyoto Protocol, which came into force in 2005 and was intended to achieve a reduction in CO₂ emissions from industrialized countries in two periods from 2005 to 2020, and the subsequent Paris Agreement in 2015 on climate change are intended to bring recognition of climate change and a commitment to countermeasures across national borders and continents. [2] In the case of the Paris Agreement the signatory states committed themselves to making efforts to prevent the global average temperature from rising +1,5 °C above the pre-industrial level of 1880–1920 and thus remain well below the agreed maximum temperature of +2 °C. To achieve this goal, net CO₂ emissions are to be reduced to zero by 2050. [3]

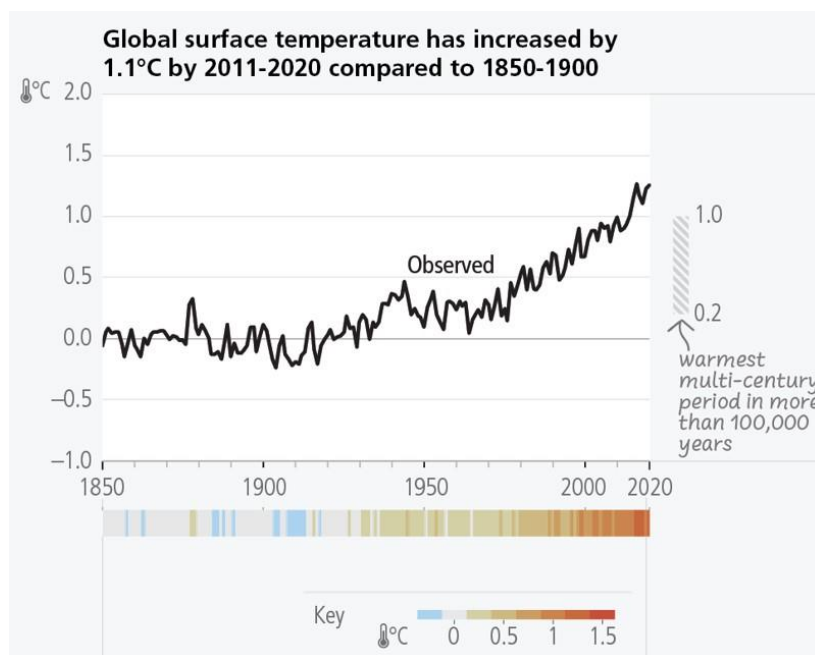


Figure 1: Average global surface temperature during the last 170 years [1]

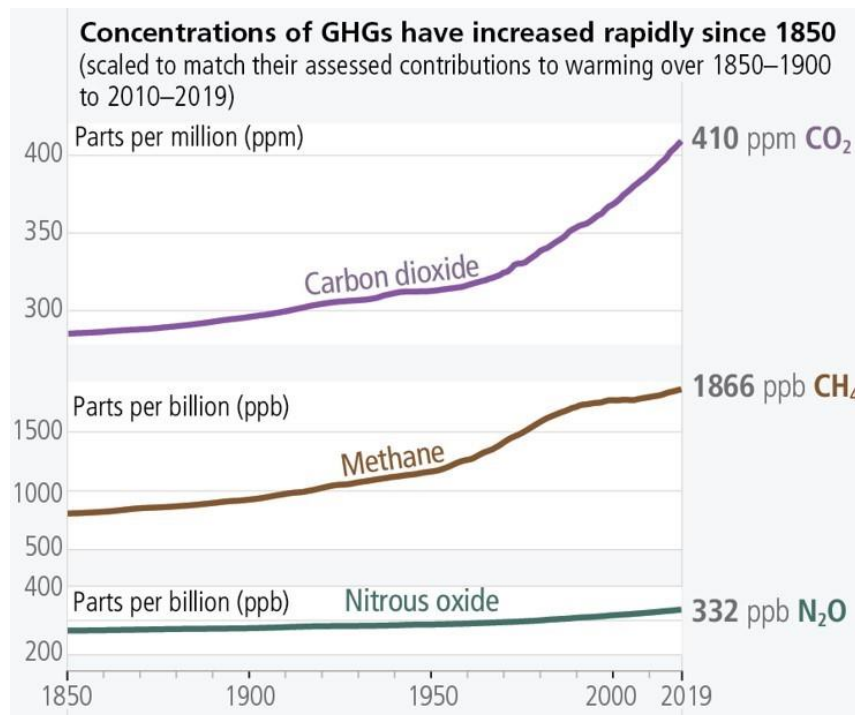


Figure 2: Concentrations of greenhouse gases during the last 170 years [1]

To achieve such an ambitious goal, a reduction of CO₂-emissions and even reaching negative CO₂-balances (carbon capture and storage) requires measures in different areas of the economy. The report "Energy in Austria" by the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology shows that 63,8% of Austria's gross domestic consumption (Figure 3) of energy sources consists of oil, gas and coal in 2022. The report also shows that the sectors energy, industry and transport produce around two thirds of Austria's greenhouse gas emissions. [4] Fossil fuels such as crude oil, natural gas and coal are not seen as CO₂-neutral energy sources because they emit CO₂ that is not part of the biosphere's carbon cycle but is usually stored underground. Therefore, fossil energy and products should be replaced by renewable resources, efficiency should be increased and overall energy and product consumption should be reduced.

To close the emerging gap left by fossil fuels, it is necessary to efficiently utilize various renewable energies and the associated energy forms. Due to a short carbon cycle in the biosphere, biomass is classified as a renewable raw material and, unlike wind, water or solar energy, it can be stored without the need for an additional storage medium. These and other factors make it possible to replace products made from fossil fuels with substitute products made from biomass.

Figure 4 shows potential processes for products out of biomass with low water content < 30%.

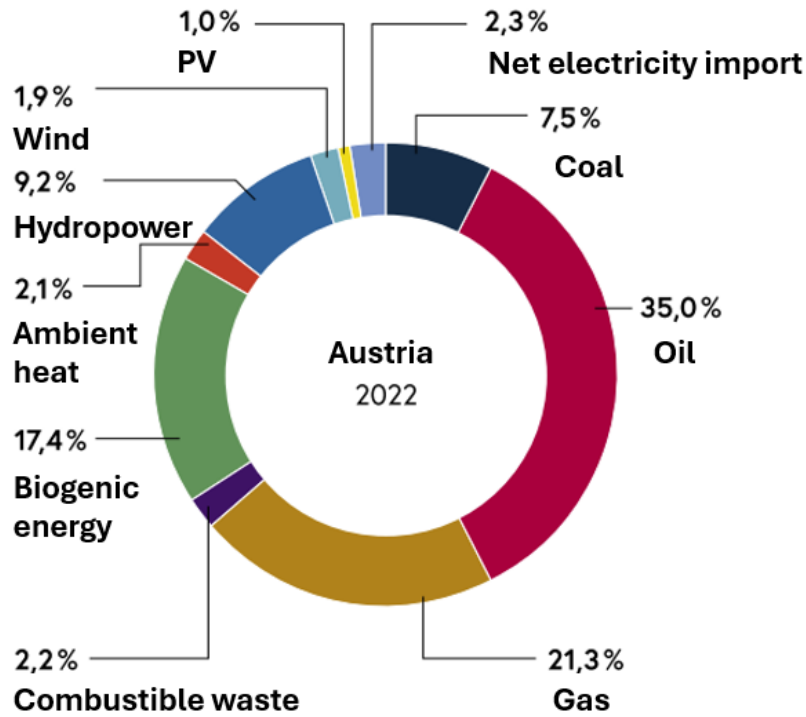


Figure 3: Gross domestic consumption of Austria in 2022, adapted from [4]

The production of heat and power from biomass by direct combustion is a common and well-established process. For applications such as transportation or in various industrial sectors, the use of biomass and biomass-based products is not yet state-of-the-art. These C-based industry sectors play a key role in the defossilization of the economy. Therefore, conversion of biomass into a secondary energy carrier in gaseous or liquid form is necessary and can take place via thermochemical or biochemical conversion processes.

The most common methods to produce biofuels for transportation are the fermentation of starch to ethanol and the transesterification of vegetable oils. In contrast, pyrolysis and gasification use thermal energy for conversion and can provide a wider range of products. Pyrolysis is carried out in the absence of air and can produce coal, liquid and gaseous products from biomass, depending on the mode of operation. Gasification is the production of an energy-rich product or synthesis gas from a solid raw material. If this process is carried out with biomass the resulting gas and following products can be seen as a substitute for fossil products. Directly after the gasification reactor the gas is referred to as product gas, whereas after gas cleaning it is referred to as synthesis gas.

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With appropriate compositions and properties of the products, it is also possible to use or feed into existing storage and distribution systems, such as the natural gas grid or the transportation fuel system. [5], [6]

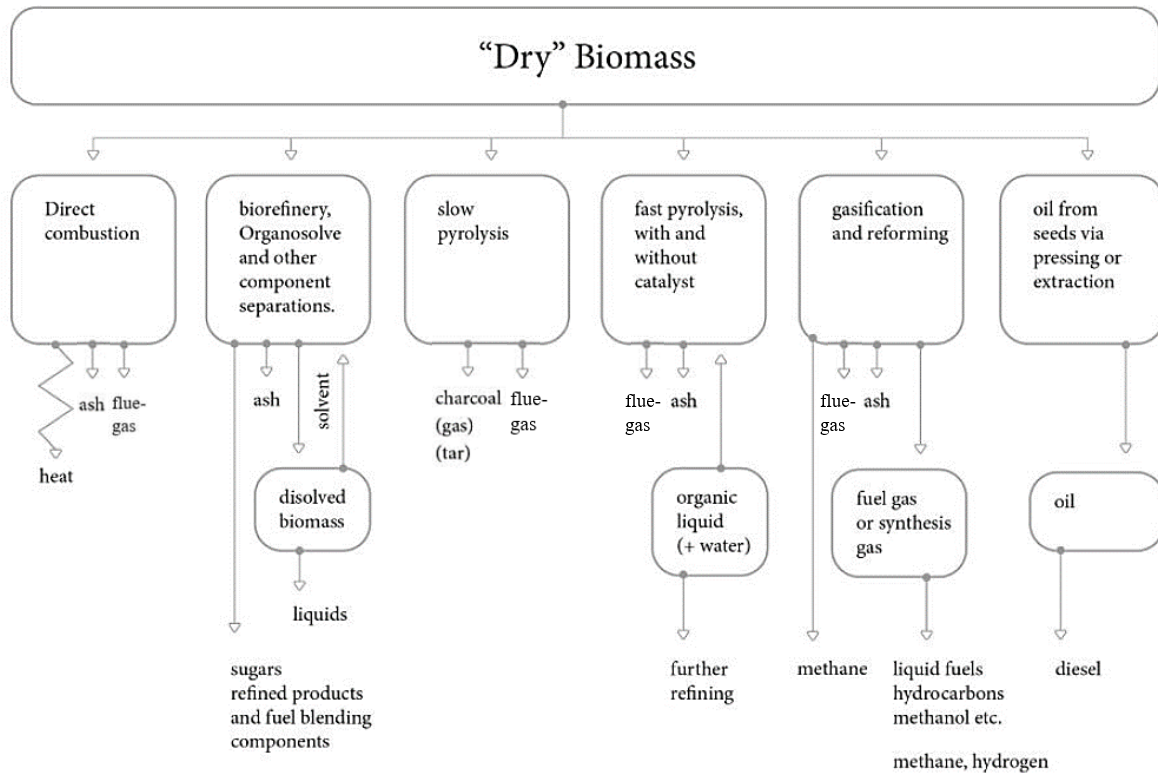


Figure 4: Overview of conversion processes for dry biomass for the production of improved fuels; adapted from [5]

Gasification and downstream gas cleaning and synthesis steps enable the production of a wide range of products. Due to the increasing interest in these mostly C-based products, various gasification methods, reactor concepts, gas cleaning processes and synthesis technologies are available or under development.

2 Principles of Gasification

2.1 Gasification technologies

Gasification is a thermochemical conversion process where solid or liquid feedstock is transformed into a gaseous secondary energy carrier, so called product gas (PG) or synthesis gas. With increasing temperature, thermochemical processes occur at the feedstock particles, including heating and drying, pyrolysis, and gasification. Unlike combustion, gasification excludes the final oxidation step to fully oxidized molecules. In gasification, the gas produced is not immediately oxidized in the combustion chamber but is utilized separately in terms of space and time. [7]

The resulting product gas consists of the main components hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), methane (CH_4) and light hydrocarbons (C_2H_4 , C_2H_6 , C_xH_y). In the case of air gasification, the proportion of inert nitrogen (N_2) also becomes part of the product gas. In addition to the main components, certain quantities of tars (condensable hydrocarbons) and inorganic components such as ammonia (NH_3) and hydrogen cyanide (HCN) are also produced during the thermochemical conversion of the feedstock. Depending on the composition of the feedstock, sulfur- and chlorine compounds may also be present in the product gas. These impurities are unintentional and can cause damage to the system and subsequent syntheses (see Chapter 2.3 Impurities).

Various gasification principles can be differentiated based on the gasification medium used, the type of heat supply and the reactor design.

Gasification medium and heat supply:

The most common gasification media are oxygen (O_2), steam (H_2O), hydrogen (H_2), carbon dioxide (CO_2) and air with 78% nitrogen (N_2) and 21% oxygen (O_2) [8]. The gasification medium used has a major influence on the resulting product gas, as various chemical reactions can take place (Table 1–Table 5) [9].

The distinction between the energy supply for gasification can be divided into allothermal and autothermal. An autothermal mode of operation provides the required energy through the partial oxidation of the components present in the reactor with the gasification medium. This makes the reactor an energetically self-sufficient system. Allothermal gasification is characterized by a separation of the process of gasification as heat consumer and the provision of heat. The energy is then fed into the gasification process via a transport medium. This can take place for example via circulating bed material or heat exchangers. [10]

Reactor systems:

The many different reactor designs can be categorized into three main groups. Fixed bed, fluidized bed or entrained flow gasifier shown in Figure 5.

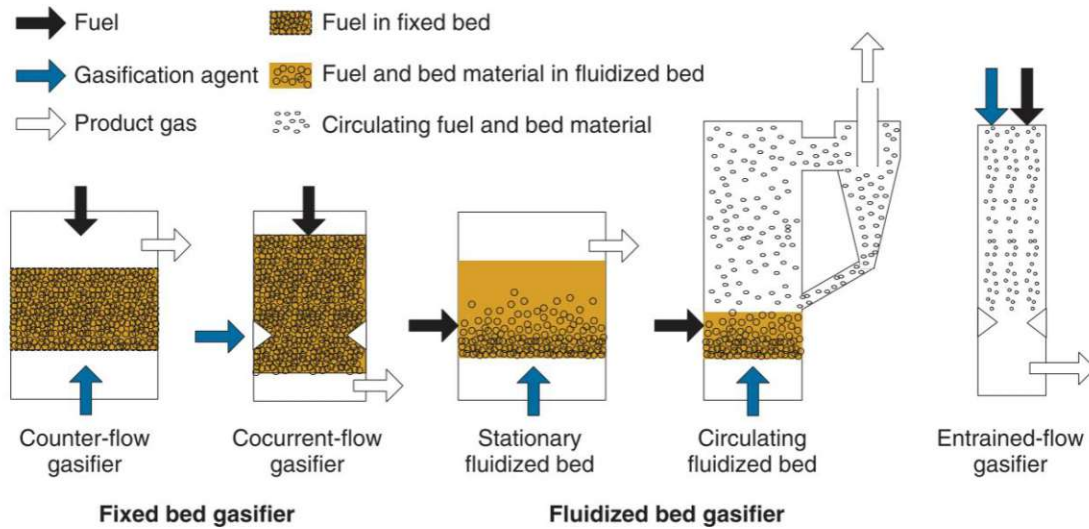


Figure 5: Overview of different types of gasifiers [10]

In fixed-bed reactors, the fuel is fed at the top of the reactor and the gasification medium is fed into the reactor using the co-current (downdraft gasifier) or counter-current (updraft gasifier) principle. Due to gravity and thermal decomposition, the fuel moves successively downwards and undergoes the processes of heating, drying, pyrolytic decomposition, reduction and partial oxidation in formed zones. Partial oxidation provides the energy for the endothermic processes. Fixed-bed reactors are therefore autothermic processes [8]. Due to the minimal mixing in the bed, it is difficult to achieve a uniform temperature distribution, fuel distribution and gas composition in these processes. Due to the different construction methods, the average tar content also differs greatly. Updraft gasifiers have a tar content of 30 to 150 g/Nm³, downdraft gasifiers 0.015 to 3 g/Nm³ [7]. Air is usually used as the gasification medium. Therefore, the gas is mostly used for heat and power production [11]. These reactor designs are mainly used in the construction of plant sizes from 10 kW to 10 MW thermal input [7].

Fluidized bed gasifiers are typically used for units between 5 and 100 MW thermal input. They contain a bed material fluidized with the gasification medium where the feedstock is directly fed into and immediately gasified. The characteristics of the fluidized bed results in very good mixing and heat distribution in the bed, which leads to a constant and uniform production of product gas. With this technology, the choice of bed material and the residence time of the gas in the reactor also have a major influence on the product gas composition. The tar content in the product gas of fluidized bed reactors is on average 10 g/Nm³ in the range between the fixed bed reactors.

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Figure 5 shows the stationary bubbling fluidized bed reactor and the circulating fluidized bed reactor with are the basic principles of fluidized bed reactors. An important reactor design based on the circulating fluidized bed is the dual fluidized bed gasifier described in chapter 2.4. [7]

Entrained flow gasifiers are typically used for large scale units with a thermal input bigger than 50 MW. In this gasification technology, the gasification medium oxygen is injected into the reactor chamber with pulverized fuel in a co-current flow. Due to very high temperatures (over 1000 °C) and turbulence in the reactor chamber, very good carbon conversion takes place, resulting in an almost tar-free product gas. However, the application of this process for biomass gasification is very limited as it is a great mechanical effort to shred fibrous biomass so finely. Also, the melting points of different biomasses can vary strongly, which can lead to technical problems in the plant, especially in this process. [7]

2.2 Gasification process on the particle

The fuel particle passes through various phases when it begins to be heated, shown in Figure 6. Depending on the type, properties and composition of the fuel, these processes can vary in intensity. The most influence have [12]:

- moisture content
- volatile matter content
- heating value
- ash content
- elementary composition

The range of volatile substances in biomass is typically around 70–85% of the raw material. For fossil feedstocks it is lower from ~50% for lignite, to 35% for hard coal. The ash content of feedstocks also varies strongly. For instance, woody biomass has contents of around 1–3%, typical non-woody biomass originated from stalk up to 12%. Waste streams like paper sludge reach ash contents above 40%.

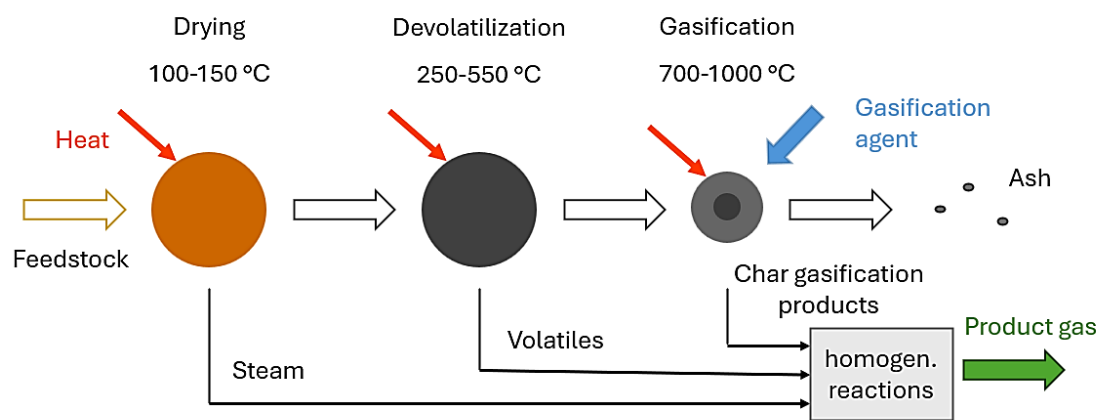


Figure 6: Stages of fuel particle gasification, adapted form [8]

After entering the reactor, the particle passes through the first phase, which is referred to as heating. The moist fuel is heated to temperatures between 98 °C and 103 °C and the contained water evaporates and the fuel dries. This process is endothermic and requires energy provided through an external energy supply. [9]

As the temperature continues to rise to 200 °C, the pyrolytic decomposition phase of the chemical structure of the organic mass begins and continues up to around 500 to 600 °C. The molecules are destroyed by the thermal decomposition. The molecules are excited by the thermal energy, causing the bonds to break. These molecular fragments can be gaseous, liquid or solid. The gaseous products (CO, CO₂, H₂, CH₄,

low hydrocarbons and other gases) leave the particle and shield it from the surrounding atmosphere. The liquid components (pyrolysis oil) consist of long-chain hydrocarbon compounds, some of which are polyaromatic, known as tars. The pyrolysis coke remains as a solid residue. It consists mainly of carbon and ash. [8]

The distribution of the various substances depends heavily on the composition of the fuel and the process conditions. The mass of gas increases as the heating rate increases, as the reaction time for pyrolytic decomposition decreases. With increasing temperatures, the decomposition of the liquid components increases and gasification reactions start to proceed. The resulting gaseous molecular fragments are in part highly reactive due to their chemical structure and react with each other or with the solid particle residues as well as with any catalytically active bed material present [13]. These reactions of primary products are called secondary chemical reactions and have a major influence on the final gas composition of the gas generation. Of great importance in this area are the water-gas reaction (6) and the Boudouard reaction (13). These reactions can be deliberately favored especially at temperatures above 500 °C, higher pressures or long residence times. [9]

The final phase of the gas generation process is gasification in the gas atmosphere. The products formed in the pyrolytic phase are now heated further and come into contact with the selected gasification medium. This results in heterogeneous and homogeneous reactions between gases and gas and solids. Depending on the gasification medium used, the reactions from Table 1–Table 5 occur with varying degrees of relevance. [8]

In steam gasification, the water-gas shift reaction (7) and the steam reforming of methane (8) and hydrocarbons (9) are particularly important for the gas composition. By varying the pressure and temperatures, the reactions can be influenced by the reaction equilibria and a certain control of the gas composition is possible, as the homogeneous gas reactions are highly decisive. [8]

Oxidation reactions involving oxygen

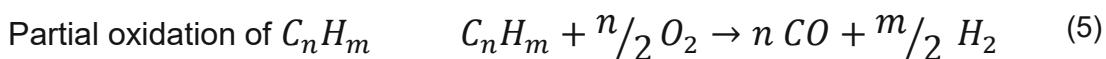


Table 1: Oxidation reactions involving oxygen; C_nH_m represents tars in general, adapted from [9]

Gasification reactions involving steam

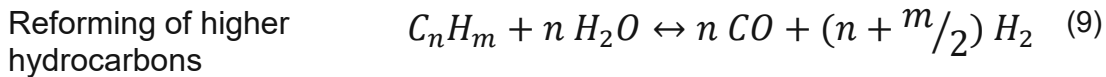


Table 2: Oxidation reactions involving steam; C_nH_m represents tars in general, adapted from [9]

Gasification reactions involving hydrogen

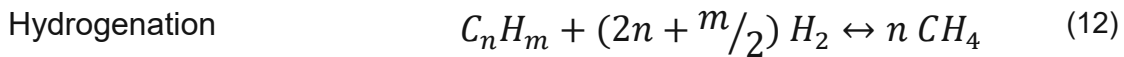
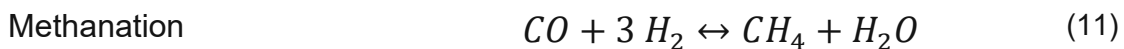


Table 3: Oxidation reactions involving hydrogen; C_nH_m represents tars in general, adapted from [9]

Gasification reactions involving carbon dioxide

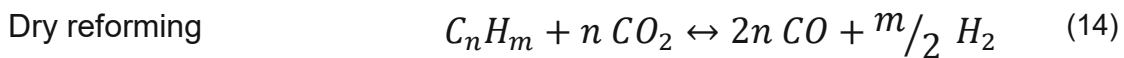


Table 4: Oxidation reactions involving carbon dioxide, adapted from [9]

Gasification reactions of tars and hydrocarbons

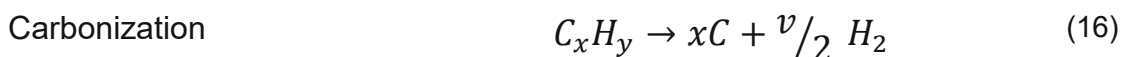
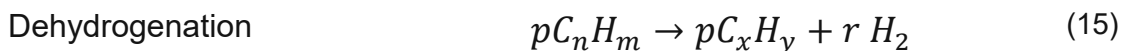


Table 5: Temperature-controlled reactions; C_nH_m represents heavier tars, C_xH_y represents hydrocarbons with a smaller number of carbon atoms or a larger degree of unsaturation than C_nH_m , adapted from [9]

2.3 Impurities

Gasification not only produces the main gas components described above, but also impurities and undesirable compounds in the gas. Depending on the fuel used, these impurities can occur in larger or smaller quantities and cause damage or problems in the plant and downstream applications. It is therefore important to lower the problematic compounds content or, if possible, to reduce or even prevent their formation.

Undesirable components are [12]

- Coarse and fine particles
- Long-chain hydrocarbon compounds, so-called tars
- Nitrogen compounds (ammonia, HCN)
- Sulfur compounds (H₂S, COS, thiophene)
- Halogen compounds (HCl, HF and others)
- Alkaline compounds (mainly sodium and potassium compounds)
- volatile heavy metals

Particles can cause erosion and clogging. Tars may condense when the product gas cools down below the tar dew point. These can then accumulate on system parts, especially cooled heat exchanger surfaces.

Sulfur, chlorine and nitrogen compounds as well as alkaline components and heavy metals can cause corrosion and lead to high emissions and environmental issues. They also cause deactivation of catalysts. For this reason, it is important to keep these components as low as possible and to largely free gas for syntheses from them. [10]

PG cleaning can be divided into coarse and fine gas cleaning. In coarse gas cleaning, the majority of the interfering impurities are separated from the PG. The gas can already be used in gas engines after these steps. If the gas is to be further cleaned so that it can be used for syntheses, impurities must be removed down to very low concentrations. This cleaning is carried out using fine gas cleaning steps. Further details will be described in the following.

Particles:

The quantity of particles in the product gas depends on the gasification reactor selected. For example, a lower number of particles is discharged from a fixed bed reactor than it would be from a fluidized bed reactor. The fluidization in the fluidized bed causes attrition of larger particles of feedstock, dust, unconverted carbon or bed material. As soon as they reach a critical diameter, they are discharged with the gas flow and must be separated.

Measures are required to separate the particles before the gas can be fed in further applications (see Table 6).

Method:	Separation range Particle diameter	Operating temperature	Particle reduction [11]
Gravity separation:			
Cyclone	>5 μm	Material dependent 200–900 °C	45–70%
Filter separation:			
Fabric filter (bag filter)	>0,5 μm	max. 250 °C	90–99%
Hot gas filter (candle filter), ceramic or metal[14]	>0,5 μm	Up to 1000 °C	
Granular bed filter[15], [16]	> 0,8 μm	~550 °C (depending on tar content and granules used)	80–95%
Electro separation:			
Dry electrostatic precipitators (ESP)	<0,1 μm and >1 μm (separation minimum 0,1–1 μm)	~500 °C	>95%
Wet electrostatic precipitators (ESP)	<0,1 μm and >1 μm (separation minimum 0,1–1 μm)	< 65 °C	95–99%
Absorption:			
Scrubber: Water, RME or similar	0,05–0,9 μm , depending on apparatus	<100 °C	40–65%

Table 6: Particle separation methods, if not marked differently cited from [8]

Cyclones can be used to remove high amounts of particles down to a particle size of 5 μm from gas. Filters form filter cakes on the filter surface on which even fine particles down to 0,5 μm can be separated. However, high particle concentrations in the gas quickly lead to a rapidly increasing pressure drop. Other pollutants can be separated on filters by adding sorbents, such as H_2S can be separated by adding sorbents containing calcium. Also, higher tar molecules can be separated in the same step, depending on their dew points [17], [18]. Precoating the filter material can also improve cleaning and extend service life. Filters can be designed as fabric filters (<200 °C), hot gas filters which can be made out of metal or ceramic (<1000 °C) or granular bed filters with temperature ranges dependent on the used granules. Granular bed filters are less susceptible to clogging compared to fabric filters and hot gas filters, but the regeneration of the granulate is difficult and disposal of the material is costly. [8]

Electrostatic separation of particles includes the separation of aerosols and mist droplets. At particle size range of 0,1 μm to 1 μm , the forces effective for electrostatic dedusting act against each other, which leads to a separation minimum in this size

range. Separation takes place at the so-called precipitation electrode, which must be cleaned to maintain its function. This can be done electrostatic pulses for the hot gas cleaning and dry particles, or water film rinsing which has to take place at low temperatures. A study conducted by Villot et. al. in 2013 showed a good separation behavior with the hot gas ESP variant at temperatures of 510 °C and 680 °C [19]. With the wet ESP tars are also separated, therefore it is difficult to dispose of the resulting mixture which has to be considered as hazardous material. A low pressure drop as well as a high flow rate can be achieved with electrostatic separation, however the investment costs are high. A great attention must also be paid to explosion protection when using electric dust extractors. [8], [18]

A major advantage of hot gas particle separation is that the gas does not need to be cooled down significantly before the filter. This prevents the condensation of most tars in this area and reduces clogging of filter pores or piping.

Scrubbers use a washing liquid to separate particles. Various apparatus can be used for this purpose like a tower scrubber, a rotation scrubber, a venturi scrubber or other scrubber types [11]. Scrubbers require an inlet temperature of lower than 100 °C in order to work correctly. Due to their low separation rate for particles and their clogging tendency, they are rarely used for dedusting. [8]

In low-temperature gas cleaning, a combination of the particle separation step with the separation of tars and other inorganic impurities is advantageous (e.g. precoating of filters for the separation of HCl), as this saves the costs of further cleaning steps. [8]

Tars:

Tars are a very important contaminant in the product gas. Condensation of tars can cause blockages and damages to the system and therefore demand a high level of maintenance.

In the official guideline for sampling and analysis of tar published by IEA Bioenergy Gasification Task, any organic compound present in product gas except gaseous hydrocarbon from C1 to C6 is classified as tar. It further specifies that tars are hydrocarbons with a molecular weight higher than benzene (78 g/mol).[20]

During the pyrolysis of the fuel particle and further heating, various tar conversions take place shown in Figure 7 and Figure 8. So-called primary tars are formed during the pyrolysis of the fuel particles at 200–500 °C and form a complex mixture of several hydrocarbon compounds for example products like ketones, alcohols or carbon acids. With increasing temperature and contact with the gasification medium, parts of these hydrocarbon compounds break down into smaller gaseous molecules. The remaining tars are converted to secondary tars, composed of alkylated mono- and diaromatics including heteroaromatics like pyridine, dioxin thiophen or furan. Above 800 °C a

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recombination of tars to tertiary tars, the aromatic hydrocarbons, begins and the total number of tar species decreases. Typical tertiary tars are naphthalene, phenanthrenes, pyrenes and benzopyrenes. These tars are also called polycyclic aromatic hydrocarbons (PAHs). [21]

A classification of tars according to molecular mass (Figure 9) is also useful, as information about the condensation behavior of tars can be derived. Larger tars (class 4–5) have a higher dew point and can condensate at higher temperatures in downstream pipes or heat exchangers. Tars of class 3 condensate to low temperatures (dew point 80–150 °C). If the temperature is decreased below this level they can cause problems in downstream applications. Although the tar classification of the IEA does not classify benzene as tar, the

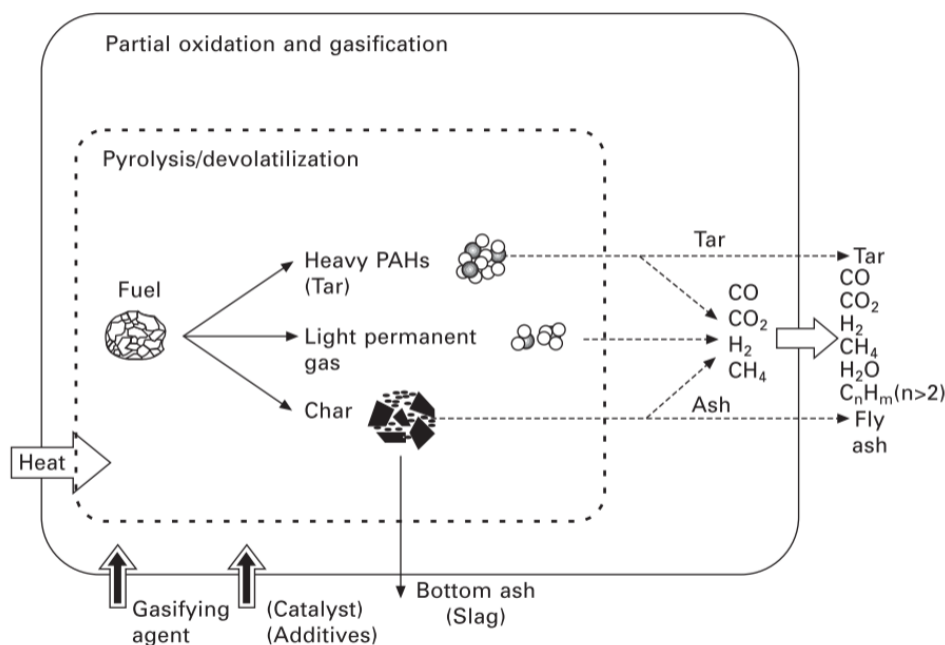


Figure 7: Tar formation through the conversion phases [9]

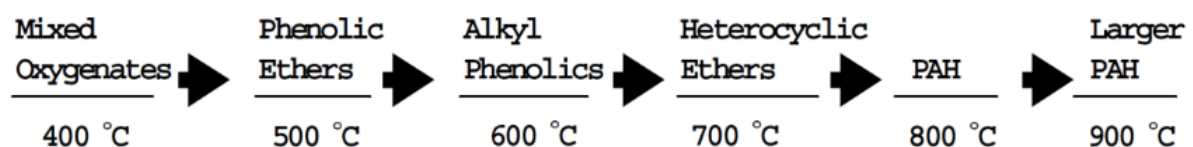


Figure 8: Tar maturation scheme [22]

Tar class	Class name	Properties	Main compounds
1	GC-undetectable	Very heavy tars, cannot be detected by GC	Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar
2	Heterocyclic aromatics	Tars containing hetero atoms; highly water-soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with single ring; do not pose problems regarding condensability and solubility	Toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2–3 rings)	2 and 3 ring compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy PAH compounds (4–7 rings)	Larger than 3 rings, these components condense at high temperatures at low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

Figure 9: Classification of Tar compounds according to physical properties and molecular weight – ECN classification [23]

condensation temperature of benzene at 80 °C also makes it highly recommendable to separate it and it is assigned to tar class 3. Those class 3 tars are represented by benzene, toluene, ethylbenzene and xylene in measurements and referred as BTEX. [23]

A further classification of tars is made by the analysis methods. The analyses in the Tar guidelines distinguish between gravimetric tars, which are calculated by weighing residues from evaporated samples, and tars that can be measured by gas chromatography and mass spectrometry so called GC/MS tars. It is important to note that no exact separation of these two tar groups can be made, as there is overlap between the tars contained in the measurement results. Furthermore, the significance of the gravimetric method is comparably low at lower tar concentrations and it is less reproducible compared to the GC method. [20]

Tars present in the product gas can be reduced in two ways. Primary tar reduction is the reduction which occurs directly in the gasifier. All subsequent cleaning steps belong to secondary reduction. Table 7 shows an overview of possible tar reduction methods. The formation, conversion and reduction of tars in the reactor are influenced by the fuel, the reactor design [24], the process conditions [17] and the catalytic effect of the components involved, such as bed material, ash and additives [13]. Devi et al. provides a detailed summary of primary measures and their effect on tar composition. [25]

Primary reductions are preferable as the tar content can be minimized from the start of the process chain. The less tar content in the PG the less complex and expensive measures must be taken for secondary reduction.

Method:	Tar reduction [26]	Operating temperature
Filter separation:		
Fabric filter with precoating	0–50%	max. 250 °C
Sand bed filter	50–97%	10–20 °C
Electro separation:		
Wet electrostatic precipitator (ESP)	0–60%	< 65 °C
Absorption [27]:		
Scrubber: RME or similar	50–90%	<100 °C
Adsorption [26], [28]:		
Fixed bed adsorber	50%	
Catalytic reduction [29]:		
Steam reforming (H ₂ O), Equation ((9))		650–900 °C
Dry reforming (CO ₂), Equation (14)		650–900 °C
Thermal cracking [29]:		
Thermal cracking or hydrocracking (steam)		>1100 °C

Table 7: Tar reduction methods, if not marked differently cited from [8]

Secondary tar reduction measures can be achieved by physical separation, thermal cracking or catalytic reforming downstream the gasifier.

Thermal cracking or catalytic reforming: By heating the PG to above 1100 °C or by contacting it with catalysts at an elevated temperature (650–900 °C), organic components are converted to H₂ and CO (equation (9)) or with the presence of steam to CH₄ (equation (14)). By using catalytic bed materials or additives (olivine, Ca-containing bed materials, or others) in the reactor (in-situ), this measure can also be assigned to the primary measures. Secondary reduction (ex-situ) with catalysts like nickel, iron based-, or zeolite based-catalysts among others also show promising results. Although some of them, nickel for example, are sensitive to deactivation by coke formation or other inorganic PG impurities. [29]

Physical separation via filtration or ESP have already been described above and are operated in a similar way compared to particulate separation.

A widely used tar separation concept is the liquid scrubbing of the PG. Packed scrubbers, Venturi scrubbers, jet scrubbers, rotary scrubbers, vortex scrubbers and bubble columns can be used as scrubber equipment. Depending on the scrubbing medium, the separation of the tars can take place via condensation by lowering the PG temperature or absorption. Water scrubbers are used for cooling the product gas, water condensation and for separating water-soluble inorganic impurities and condensing tars. The separation of tars in water scrubbers is very limited and although

water is a cheap washing media, the disposal of wastewater heavily contaminated with organic hazardous substances is difficult and expensive. For this reason, scrubbers with oily scrubbing liquids are increasingly being used. Separation by condensation and adsorption leads to better separation results. In tests with rapeseed oil, heating oil and rapeseed methyl ester (RME) as media, Hofbauer et. al (2000) identified RME as a suitable medium with high naphthalene solubility [30]. Operating costs of scrubbers are high because of the used solvent liquid and could be significantly reduced by regenerating scrubber media. [31], [8]

The OLGA technology uses a three-step system of scrubbers with operating temperatures above the water dew point. The first scrubber cools the PG and transfers it to another scrubber that absorbs tars and whose medium can be regenerated with hot gas. The waste streams from the first scrubber and the loaded gas can be used as additional fuel for incineration. [32]

Since all above mentioned tar separation measures have limited reduction efficiencies especially with class 3 tars, it might be important to use an additional method for fine gas cleaning. Combinations of the gas cleaning steps already mentioned and downstream adsorbers for different impurities are state-of-the-art [33]. Adsorption is a widely used method to remove remaining amounts of impurities out of PG with very different adsorption materials. Activated carbon is an interesting medium for tar reduction due to its regeneration properties. Research is being carried out to replace scrubbers for the separation of low tar concentrations with temperature swing adsorption applications. [34], [35]

Nitrogen-Compounds:

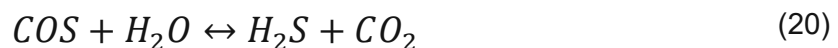
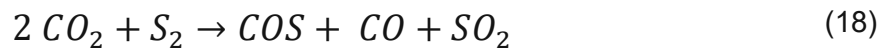
The formation of nitrogen components in the product gas is highly dependent on the nitrogen found in the fuel. The following compounds occur in varying concentrations: nitrogen (N_2), ammonia (NH_3), hydrogen cyanide (HCN) and isocyanide oxide (HNCO). The separation of nitrogen compounds is particularly important, as it leads to high nitrogen oxide values during combustion and counts as a catalyst poison in most synthesis processes.

Currently, NH_3 is mainly separated via scrubbers. Due to the water solubility of NH_3 and HCN, a separation of more than 99% can be achieved by using water scrubbers [36]. Scrubbers with organic solvents in which the water from the PG also condenses achieve an NH_3 separation rate of around 50% [37].

Catalytic decomposition of nitrogen compounds can be observed in hot gas cleaning processes. Abdoulmoumine et al (2015) provide an overview of various catalyst test studies that can be used for N-component separation at temperatures between 450 and 750 °C. Nickel- and iron-based catalysts are particularly effective. [29]

Sulfur-compounds:

The proportion of sulfur components in the PG is influenced by the fuel, the gasification technology and the operating conditions. Differences in the S content of fuels can already be seen in woody biomass. Bark or coniferous components have a higher content than stem material [38]. During gasification, sulfur is mainly converted into hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), mercaptanes (CH_3SH) and thiophene (C_4H_4S). [39] H_2S is primary formed through the reduction of sulfur compounds in the fuel. COS is formed by chemical reaction of H_2S , S_2 or CS_2 through the reactions (17) - (19). The ratio of H_2S to COS compounds due to reaction (20) depends on the process conditions, the gasification medium and the catalysts present. [40]



Components such as mercaptans and disulfides are largely converted to H_2S by the effect of temperature during gasification. However, COS , H_2S , thiophene (tar with S-compound) and minor components can remain in the PG. [39]

The reduction of sulfur compounds can take place primarily in the gasification reactor and secondarily in downstream gas cleaning. Primary reduction by adding calcium-based sorbents such as limestone or dolomite to the reactor chamber can bind sulfur chemically. The resulting product, calcium sulphate $CaSO_4$, is stable and classified as environmentally friendly. [41]

Secondary reduction methods are implemented as wet or dry gas cleaning methods. A distinction can also be made between physico-chemical absorption and adsorption processes.

For the separation of sulfur from PG, an adoption of processes from coal gasification can be made. Several wet solvents and different process designs are used, for example:

Amine scrubbers can remove H_2S (up to 99%) and CO_2 (up to 30%) from the gas stream. The scrubbing solution (MEA (monoethanolamines), DEA (diethanolamines), MDEA (methyldiethanolamines)) is fed through packed apparatus in counterflow to the gas and regenerated again in a second step by heating. COS cannot be separated with these media. Pre-staged hydrogenation of the COS would also be necessary. In addition to the S-components, HCl is also separated in this step.

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Alkaline scrubbers usually use potassium carbonate and sodium carbonate for pressurized (20–70 bar) scrubbing. In this process, H₂S, HCl and CO₂ can be removed to levels below 0,1 ppm. Again, regeneration of the solvent is used after scrubbing.

The Rectisol process uses methanol as a solvent at temperatures from –40 °C to –80 °C. In this process, H₂S and CO₂ can be separated to low ppm. COS, HCN, mercaptans and HCl are also separated. The disadvantage of this process is its high complexity, which means that it requires costly equipment and high investment costs.

Other solvent-based processes are summarized by Bridgwater et. al. 2009. [11]

Adsorbers are mainly used for fine gas cleaning of the PG for syntheses (<50 ppm sulfur content). Zinc oxide is normally used as guard beds but copper-based, alkaline earth metal-based, nickel-based sorbents or active carbon with doping can also be used for sulfur removal. [29]

Hydrogen halides-compounds:

The amount of hydrogen halide components results from bound nutrients in the biomass or from impurities in the fuel. Some alkali metal compounds condense when the gas cools down and can be separated on filters. Other gaseous hydrogen halides especially chlorine compounds (HCl) are usually removed using scrubbers. Either water or caustic solutions are typically used. Fine gas cleaning down to <0,01 ppm can be reached by using adsorption with alkali or alkaline earth metal sorbents. [29]

2.4 Dual fluidized bed (DFB) steam gasification

The dual fluidized bed (DFB) steam gasification technology is an innovative technology for the efficient conversion of carbon-containing raw materials into valuable product gas. A typical composition of the DFB product gas is shown in the Table 8.

Components	Quantities	Units
H_2O	30–45	vol%
CH_4	10–11	vol% (dry)
C_2H_4	2–2,5	vol% (dry)
C_3 fraction	0,5–0,7	vol% (dry)
CO	24–26	vol% (dry)
CO_2	20–22	vol% (dry)
H_2	38–40	vol% (dry)
N_2	1,2–2,0	vol% (dry)
H_2S	130–170	ppm _v (dry)
NH_3	1100–1700	ppm _v (dry)
tar	2–5	g/Nm ³ (dry)
Particulates	20–30	g/Nm ³ (dry)
LHV	12,9–13,6	MJ/Nm ³ (dry)

Table 8: Typical composition of product gas from DFB gasification of woody biomass before gas cleaning [37]

As bed material in the DFB process different materials can be used. Commonly used are the catalytically active material olivine, a naturally occurring magnesium iron silicate [42], silica sand [43] or limestone [44].

Figure 10 shows the overall scheme of dual fluidized bed gasification, which, as the name suggests, is based on two connected fluidized bed reactors, the gasification reactor (GR) and the combustion reactor (CR). Feedstock is fed into the bubbling fluidized bed gasification reactor and gets mixed into the fluidized bed material at 800–850 °C. Due to the intensive mixing and the good mass and heat transfer in the fluidized bed, the particle passes through the process of drying, devolatilization and char gasification in a very short time, so that no differentiation between the phases defined in chapter 2.2 is possible. Reactions with steam as gasification agent take place. The product gas consists of the main components hydrogen, carbon monoxide, carbon dioxide, and methane. Since the gasification process is endothermic, energy must be supplied to the process. This is achieved by transporting part of remaining char particles together with bed material into the CR via a connection at the bottom of the GR. In the combustion reactor, the residual carbon or char is burned by fluidization

with air which heats up the bed material to 900 °C to 950 °C through the exothermic reaction. As the fluidized bed in the CR is a fast-fluidized bed, the hot bed material is entrained together with the gas stream and is fed back into the GR after being separated from the flue gas stream in a cyclone. To prevent an air or gas slip via the connection from GR to CR, sealing gas (steam) is usually used. Depending on the defined system boundary, the process can be characterized as allothermic or autothermic. [8]

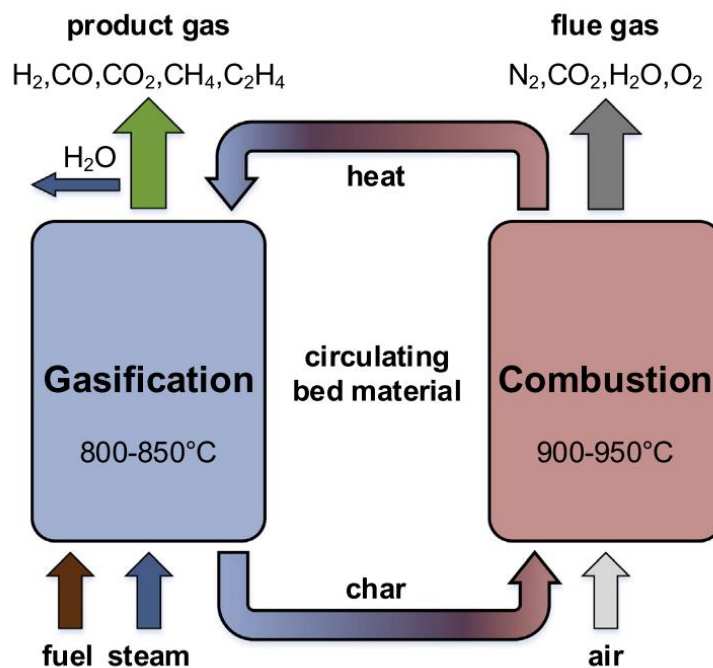


Figure 10: Basic principle of the DFB steam gasification process [45]

In the last three decades, the development of DFB gasification has been strongly advanced, leading to the market maturity of the DFB technology. It is therefore already an established technology for gasification with woody biomass on an industrial scale. Plants in Güssing [46] and Oberwart (Austria) as well as in Senden, Germany (Figure 11), and Gothenburg, Sweden (Figure 13), have used this process to produce product gas in capacities from 8 to 33 MW thermal energy input. The plants in Güssing, Oberwart and Senden were built for combined heat and power (CHP), while the plant in Gothenburg, known as the GoBiGas plant, was built for demonstration of biomethane production via gasification and downstream methanation. [47]

Güssing as well as Oberwart used high quality woodchips as feedstock, which started to cause economic difficulties once wood prices started to significantly rise due to increasing demand. It was necessary to consider other feedstocks with lower quality. Senden was the first industrial scale plant that used logging residues as lower quality

biomass [48]. At GoBiGas wood pellets, wood chips, shredded bark and reconverted wood were tested. [33]

All four plants are built based on the same reactor design (Figure 12) and use heat exchangers downstream the GR for gas cooling down to 150–200 °C, a fabric filter for separating particles and a rapeseed methyl ester (RME) scrubber for removing tars. In Güssing, Oberwart and Senden, the gas was burned in combustion engines after the 2-stage gas cleaning. In the GoBiGas plant, further gas cleaning was necessary for methane synthesis, described further in chapter 2.6.

Experience reports on the Senden plant by Kuba et. al. [48] and the GoBiGas plant by Larsson et. al. [33] address the difficulties encountered with the plants and the improvements made. Reducing the tar content in the gas is one of the most important measures to protect downstream plant components from fouling and clogging. Both plants experienced problem with the product gas heat exchangers after the GR due to condensation of tars. Therefore, a focus is laid at important product gas related points in the following paragraphs.

The asymmetric GR design has an inclined, non-fluidized wall (see Figure 8). With the help of cold model tests, it was shown that this area is poorly fluidized and that the material in this section of the reactor behaves as a moving bed. Due to the low presence of the gasification medium in this zone, the components produced there can only react to a limited extent, which leads to an increased tar content in the product gas. In Senden, additional nozzles were therefore installed in the area of the inclined wall. A significant reduction at the gravimetric tar content was observed. [48]

The water content of the biomass was identified as an important point for constant plant operation and PG quality. In the Senden plant, a separate drying system was used and optimized, which led to an improvement in the gas composition. GoBiGas and Güssing had no implemented drying system.

In all plants, additives were fed into the gasification process to enhance the effect of the bed material with catalytically active substances. While in Güssing, Oberwart and Senden calcium was added to the process in the form of calcium carbonate or calcium hydroxide, GoBiGas used potassium in form of K_2CO_3 dissolved in water (40 wt.-%). Senden also reused activated olivine by shifting out discharged material from the gasifier bottom. These measures have significantly reduced the tar content in all plants.

These experiences and the need to consider low quality feedstocks and waste streams led to further developments in the reactor design and downstream product gas cleaning applications. The last significant change to the reactor design was developed at the TU Wien. In a 100 kW pilot plant a countercurrent column was implemented in the gasifying reactor. The reactor design is shown in Figure 12 on the right site in

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comparison to the conventional design on the left side. The aim of implementing the countercurrent column is to increase the contact time of the gas and the tars it contains with the hot catalytic bed material. As a consequence, tars are reduced by reforming and cracking reactions in the gas phase in the presence of the catalytically active bed material. [45], [49]

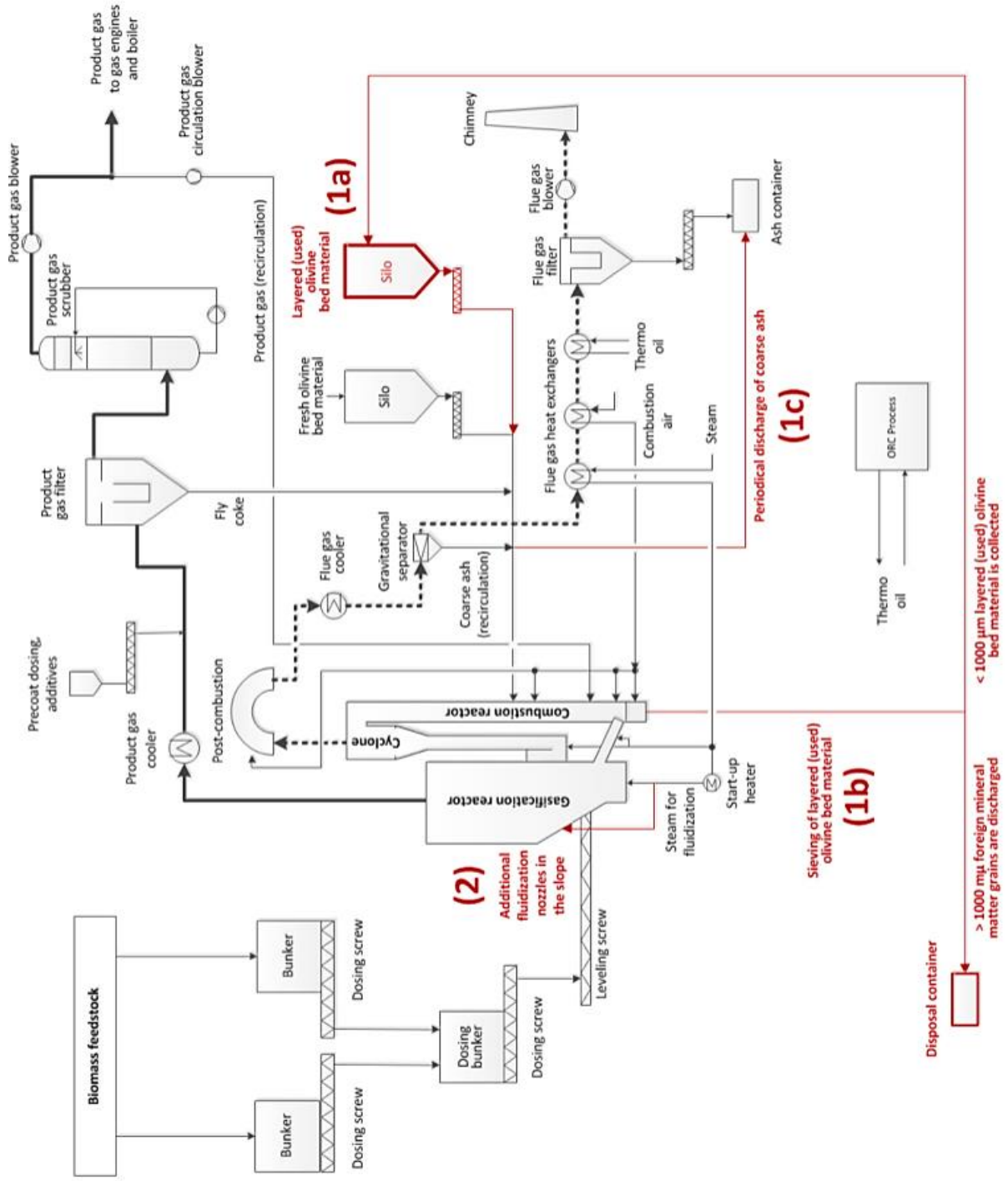


Figure 11: Simplified schematic of the CHP Senden plant, Red lined: Optimization measures [47]

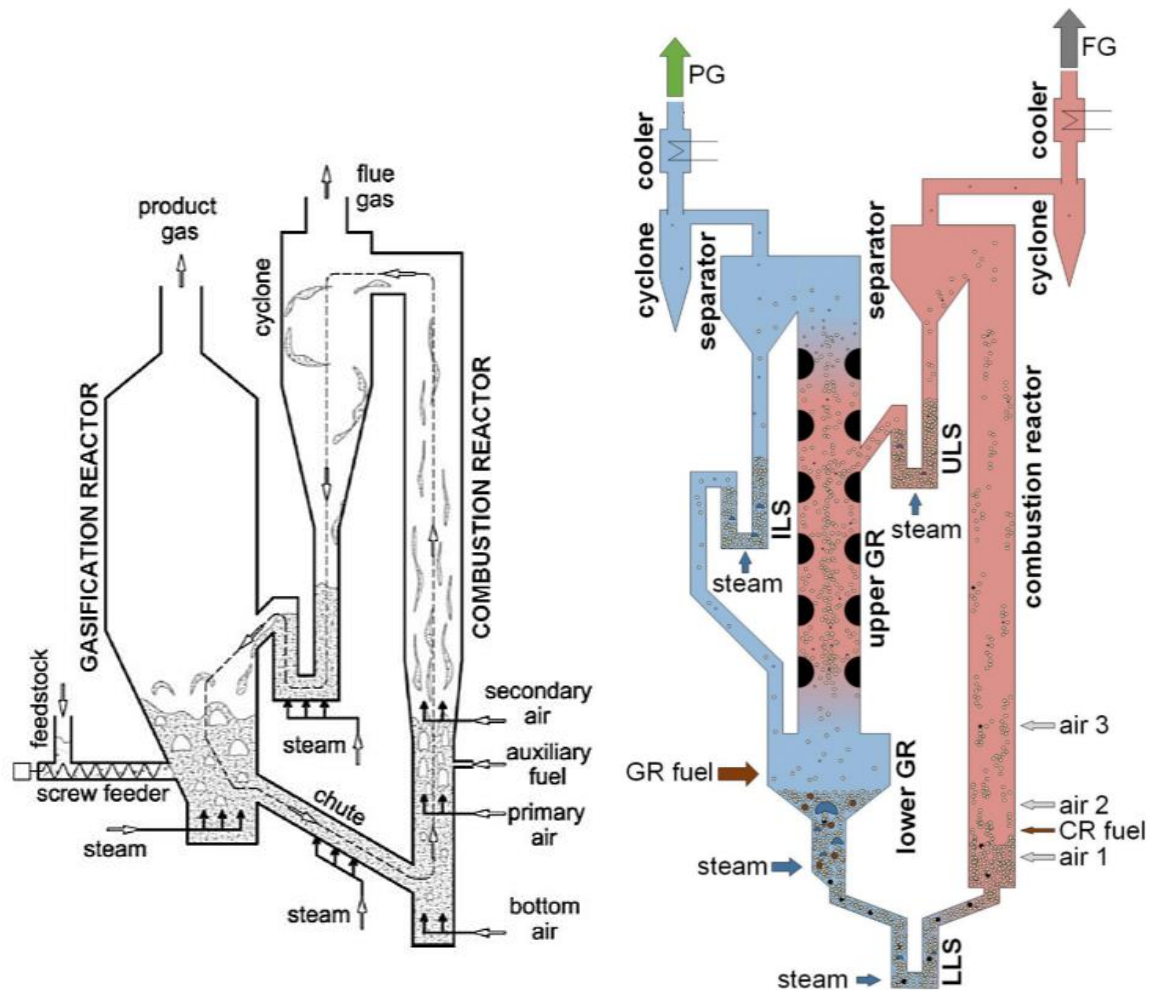


Figure 12: left side: conventional reactor design used in Güssing, Oberwart and Senden[48]
 right side: new reactor design with counter current column in GR at 100 kW plant located at TU
 Wien; ILS: Internal loop seal, ULS: Upper loop seal, LLS: Lower loop seal [45]

The upscaling step of the gasifier developed from TU Wien was carried out by the construction of a 1 MW demonstration plant by the company BEST - Bioenergy and Sustainable Technologies GmbH and is currently being investigated in the frame of research work performed on-site.[50], [51], [52], [53] The upscaling of the gasifier as well as the manufacturing and erection of the plant was performed by SMS group.

During the construction of the demonstration plant, BEST also further investigated the development of the gas cleaning. The further development is examined in more detail in chapter 3.1.

2.5 Synthesis of product gas

The different operating modes and reactors described in 2.1 have advantages and disadvantages for their application. However, if you want to process the gas into special synthesis products, the product gas must fulfill certain requirements depending on the desired synthesis:

- a certain H₂:CO ratio
- low inert gas content
- a certain proportion of methane and higher hydrocarbons
- very low particulate matter and tar components
- practically free of catalyst poisons (alkaline components, sulfur-, nitrogen- and chlorine components)

Prepared, cleaned gas is called synthesis gas (syngas) and consists mainly of hydrogen and carbon monoxide and smaller amounts of CO₂ and CH₄. Many processes require an exact ration of H₂ to CO, such as 2:1 for Fischer-Tropsch (FT) synthesis (conversion of syngas to liquid hydrocarbons) and 3:1 for methanation (conversion of syngas to methane). If this ratio can be provided by the gas production process, it is not necessary to use a separate water gas shift unit to produce the desired ratio. [54]

A low content of inert gases is important so that the conversion reactions can take place correctly and there is no dilution of the synthesis gas.

To avoid deactivation of the used catalysts, it is important to remove catalyst poisons from the gas. Depending on the synthesis process, sulfur, chlorine and nitrogen components as well as organic impurities known as tars must be separated to very low concentrations in various cleaning steps. Gasification processes with low concentrations of impurities help to reduce the gas cleaning effort. [10]

Impurities	Removal level for gas engine	Level for Syntheses
<i>Particles</i>	< 50 mg/m ³	< 0,1 mg/m ³
<i>Particle size</i>	< 3 μm	n.l.
<i>Tar content</i>	< 100 mg/m ³	< 0,1 mg/m ³
<i>Alkali content</i>	< 50 mg/m ³	< 10 ppbv
<i>NH₃ content</i>	< 55 mg/m ³	< 1 ppmv
<i>S- content</i>	< 1150 mg/m ³	< 0,1 ppmv
<i>Cl- content</i>	< 500 mg/m ³	< 0,01 ppmv

Table 9: Requirement-specific information for the synthesis gas quality; n.l.: no information [8]

2.6 Gas cleaning of DFB plants

As can be seen from the previous chapter, the requirements for product gas vary greatly depending on use. The scope of each plant is also slightly different and adapts to the tasks. In the Güssing, Oberwart and Senden plants, the gas was processed for use in the gas engine, which involves very manageable PG cleaning compared to the synthesis process at GoBiGas plant. Table 10 shows an overview of the plants.

	Güssing [46]	Senden [48]	GoBiGas [55]	100 kW - TU Wien [56]	1 MW Pilot plant - Simmering
Reactor design (Figure 12)	conventional	conventional	conventional	new	new
Utilization	Gas engine	Gas engine	Methanation	Research	FT- Demonstration, Research
PG cleaning:					
Gravity separator	-	-	-	✓	~
Cyclone separator	-	-	-	✓	✓
Filter (-material)	fabric	fabric (precoated)	fabric (precoated)	-	ceramic
Scrubber	RME	RME	RME	-	Water, RME
Further fine gas cleaning	-	-	✓	-	(smaller sizes)

Table 10: Overview of the reactor design used, the gas utilization and the structure of the PG cleaning of the plants Güssing, Senden, GoBiGas, 100 kW - TU Vienna and the 1 MW pilot plant Simmering

The PG quality after the gas cleaning steps of Güssing and Senden already described in Chapter 2.4 meets the requirements for the gas engine, but is not suitable for syntheses. Particles, tar-, sulfur-, N- and Cl- concentrations are still above the synthesis limits given in Table 8.

GoBiGas was used for the technology demonstration with the aim to make the owners Göteborg Energi AB and the city of Gothenburg independent of fossil fuels in the transport sector. Due to the development of the fossil methane price and the production costs of methane via the GoBiGas plant, the plant was shut down in 2018. However, it could be recommissioned depending on methane price developments [55]. The

gasification plant was built with gas cleaning and subsequent methanation shown in Figure 13. The plant includes the following steps [33]:

1, gasifier; 2, combustion chamber; 3, cyclone Flue Gas (FG); 4, post-combustion chamber; 5, raw gas (PG) cooler; 6, raw gas (PG) filter; 7, rapeseed methyl ester scrubber; 8, carbon beds; 9, flue gas train; 10, fuel feeding system; 11, product gas compressor; 12, hydration of olefins and COS; 13, H₂S removal; 14, guard bed; 15, water-gas shift reactor; 16, pre-methanation; 17, CO₂ removal; 18, methanation; and 19, drying of biomethane

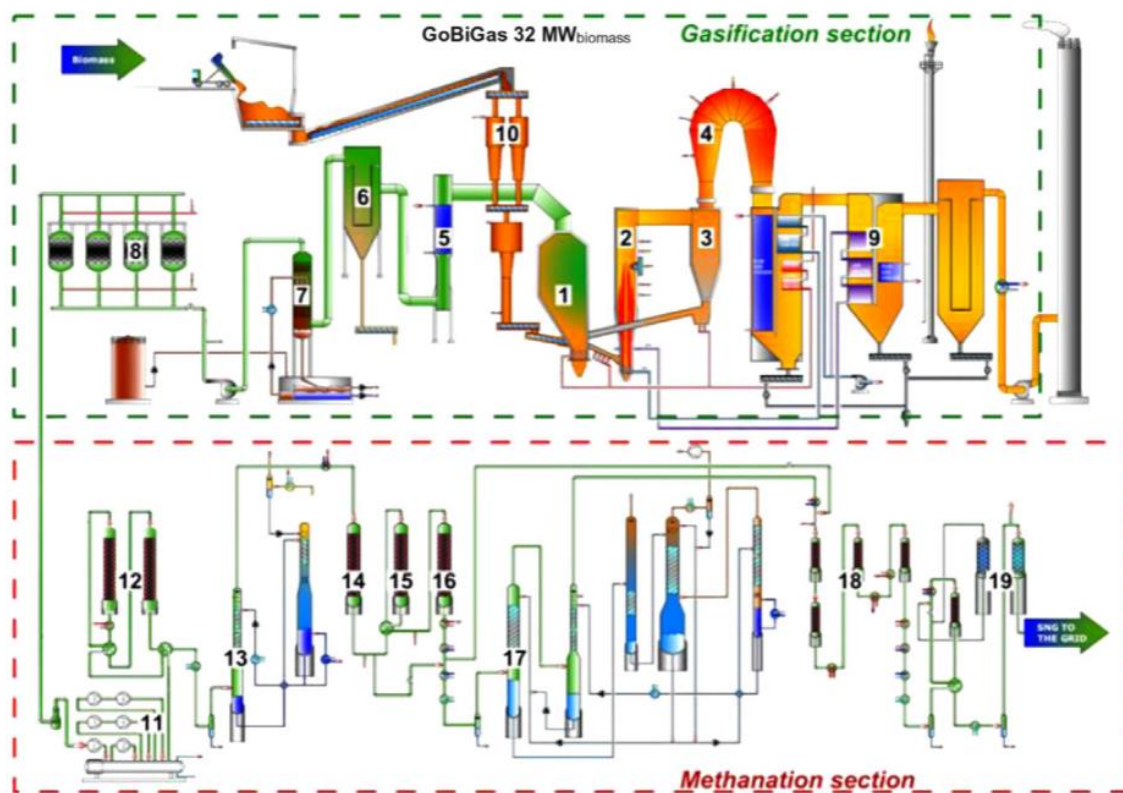


Figure 13: Process schematic of the Gothenburg Biomass Gasification (GoBiGas) biomass to biomethane plant [57]

A distinction is made here between the gasification section and the methanation section. The coarse gas cleaning is completed with step 7 and, like Güssing and Senden, includes a PG cooler, filter and scrubber. RME is also used as the scrubbing medium and similar temperatures are used. Whereas in the other plants the gas is utilized in gas engines, in the GoBiGas plant it is purified as fine gas. Residual tars such as parts of naphthalene and above all BTEX (benzene, toluene, ethylbenzen and xylene) are separated by adsorption via four activated carbon beds. One adsorber is always regenerated alternately. Despite these separators, very small quantities of PAH were still found after the activated carbon, but did not cause any problems with the compressors. The gas is then compressed to 16 bar and gas conditioning with hydrogenation of olefins and COS is carried out.

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The separation of H_2S takes place via an amine scrubbing with a subsequent zinc oxide police filter. A water-gas-shift reactor is then used to ensure the correct $H_2:CO$ ratio for methanation and leads on to methanation. As this is not covered in this thesis, further details are available from Thunman et. al. (2018). [58]

2.7 Aim of the work:

The composition of fuels is directly linked to the formation of impurities. Thus, high quality wood chips are a very clean fuel compared to other biomasses or even waste fractions but the interest in cheaper fuels or the disposal of problematic materials such as sewage sludge leads to the necessary gas cleaning and further developments in this field.

In this thesis, a first analysis of the gas cleaning of the 1 MW demonstration plant from BEST will be undertaken and the results of the fuels tested in the first four campaigns will be compared.

- How do impurities behave over the PG path, starting in the fluidized bed – Freeboard, up to the end of the product gas path?
- What separation rate can be determined for the different gas cleaning stages? Are there differences between the feedstocks?

Comparisons are also made with the results of the reduction of impurities after the conventional plant setup and the 100 kW plant at the TU Wien.

3 Materials and Methods

This chapter contains a more detailed description of the 1 MW demonstration plant of BEST GmbH located at the Syngas Platform Vienna at Simmeringer Haide, Vienna and comparisons with the 100 kW plant at TU Wien, the Güssing Plant and the GoBiGas Plant of Gothenburg, with particular focus on the gas cleaning systems.

3.1 1 MW DFB Demonstration plant



The 1 MW plant was built from 2019 to 2022 by the company SMS group in the frame of the COMET research project Waste2Value under the project lead of BEST - Bioenergy and Sustainable Technologies GmbH to scale up the further development of DFB technology and to take further development steps in gas cleaning. The plant is used to demonstrate and research the conversion of biomass residues and waste streams into a high-calorific gas with the improved reactor design described in Chapter 2.4. The plant is located on the Syngas Platform Vienna of BEST - Bioenergy and Sustainable Technologies at the Simmeringer Haide in Vienna and was commissioned in January 2022.

Since the system was commissioned, five test campaigns with an average operating time of four weeks each have been carried out. First experiences about the

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performance evaluation of the commissioning, the tar behavior over the counter current column have already been published by Hochstöger and Huber. [24], [59]

In Figure 14 an overview of the process design is shown. Centerpiece of this plant is the continuously operating dual fluidized bed gasifying process (DFB), described in chapter 2.4. The GR is divided into two areas, the fluidized bed with the freeboard area and the countercurrent column (CCC). The CCC aims to bring the produced gas back in contact with hot, catalytically active, bed material. In contrast to the six constrictions of the 100 kW system, it only has five constrictions.

The gasification process is endothermic, which means it needs an input of external energy to perform. This energy gets generated in the second reactor, the combustion reactor (CR). Via a chute the bed material (olivine) and the solid residues of feedstock (char) is transported from the ground of the GR into the CR. The olivine gets heated up during the combustion process in the CR and parts of it entrained from the reactor continuously because of the gas flow rate. A cyclone separates the bed material particles from flue gas and the hot olivine enters the GR again to deliver the needed energy.

The entry point of the feedstock into the lower part of the GR was specially built vertically above the fluidized bed. This design prevents direct contact of the feed material with the reactor wall and a possible associated local buildup of stuck material, especially when liquid or temperature-sensitive fuels are used. Also, it eliminates problems associated with material damage and clogging during in-bed feeding that were observed in the Senden plant [48]. The entire reactor system is completely refractory lined to keep energy losses as low as possible.

The lower part of the GR is used for the gasification process with temperatures around 750 °C to 850 °C. The inserted feedstock falls onto a fluidized bed of olivine particles. The overheated steam with a temperature of about 400 °C gets injected through ten lances that reach into the fluidized bed and are arranged in a circle for optimal distribution. The gas-vapor mixture leaving the fluidized bed enters the freeboard above the bubbling fluidized bed where further gas-phase reactions occur. The CCC creates a gas holdup which should have a positive influence on these reactions. The catalytic contact of the gas with the bed material is also increased by the flow downwards the CCC, which contributes to a primary reduction of impurities. Tars can be cracked into lighter fractions or CO and H₂ through steam and dry reforming reactions take place, described in the previous chapter.

The PG leaves the GR and enters a radiation cooler. The gas-carrying pipe is water cooled. The interstitial space is filled with water up to a certain level, which can be regulated in the second part of the cooler depending on the measured temperature of the gas between those parts. The deflection of the gas flow in this cooler results in a

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certain degree of particle separation by gravity separation. The particles, mainly bed material, are fed back into the reactor system via screw conveyors. The gas leaves the radiation cooler at 350–450 °C and flows into a cyclone where fly char and particles are separated and returned to the CR. The small solid particles remaining in the PG are separated in the following hot gas ceramic filter. The ceramic candle filter contains 78 filter candles which are arranged in a grid pattern and are fed from the outside. The filter cleaning happens by pressure pulsation (3–4 bar) with nitrogen and the filter cake is also transported back to the CR. After this step the hot product gas flows into a quench and scrubber system. In the first scrubber the gas is quenched with water, in the second scrubbed with rapeseed methyl ester (RME). The quench has a simple design, which helps to avoid deposits and blockages. In the apparatus, through which the gas flows from above, there are first 3 full cone nozzles radially distributed on the reactor wall with a 90° spray angle to the gas flow. This is followed by two full-cone nozzles arranged one after the other in the center of the apparatus with spray direction in the direction of flow. In the RME scrubber, the gas flowing in from below is sprayed with RME via a full-cone nozzle arranged centrally at the top. Built-in lamella plates are used as droplet separators and gas distributors. Due to the cooling of the gas from 400 °C down to 35 °C in the quench and 20 °C in the scrubber, heavier tars with dew points above this temperature condense and are collected in the two scrubbing liquids. A small amount of RME is added to the water in the quench to prevent pipes from becoming blocked with tar. The contaminated water and the RME are drawn off and fed into two phase separators, where density differences help to separate the liquids. By means of communicating vessels, the height of the contaminated layer in the phase separators is kept constant and can be drawn off. This contaminated mixture of tars, water, and RME is returned to the CR and burned. Due to this separation an addition of fresh water and RME is necessary. This exchange is intended to prevent saturation of the RME with tars, in particular naphthalene. The coarsely cleaned product gas has a temperature of about 40–50 °C and passes the product gas fan. This blower moves the gas through the whole cleaning and cooling process and delivers it to the sample and online test station. With the aid of a downstream recirculation blower, a small part of the product gas can be recirculated to the CR to control the temperature in the CR. At this point, partial product gas streams can be transferred to fine gas cleaning with a following Fischer-Tropsch demonstration plant [60], and other smaller research facilities. The excess gas flows into a post-combustion chamber where the product gas is burned and the product gas line ends.

At the bottom of the GR a chute into the combustion reactor is installed. The olivine and solid feedstock residue mixture slips into the CR as bed material and ash are discharged from the CR. Two steam nozzles create a gas barrier in the chute to prevent air slipping from the CR into the GR. An air or exhaust gas slip in the GR would cause oxidation reactions in the PG and greatly reduce the quality.

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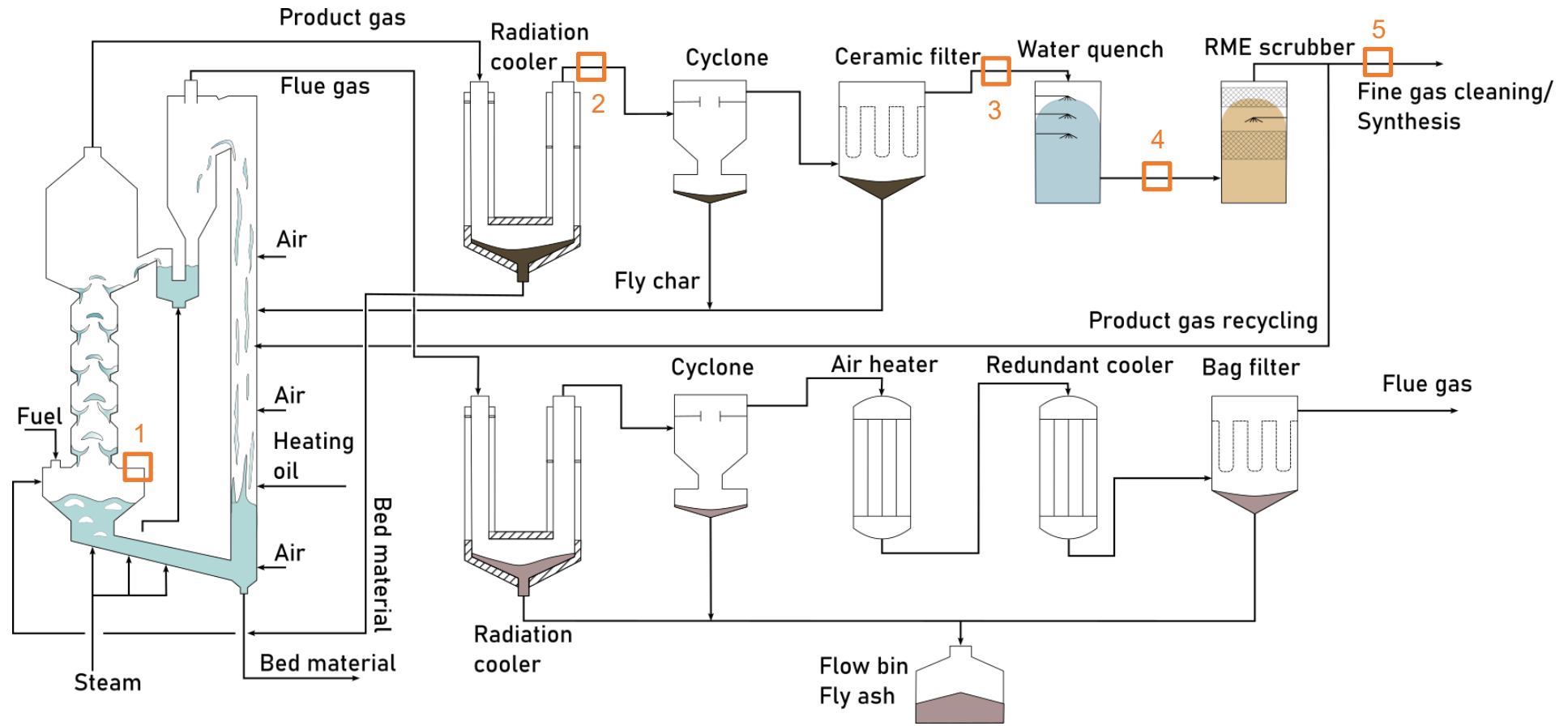


Figure 14: Overview of the gasification demonstration plant including DFB gasifier, PG cleaning, FG cleaning, recirculation of streams; Red marked areas are PG measurement points: 1 - PG freeboard gasifier, 2 – PG after radiation cooler, 3 - PG after hot gas ceramic filter, 4 - PG after quench, 5- PG after RME scrubber

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In the combustion reactor air is used as fluidizing gas and full oxidation of the char particles is achieved. Through this process, the bed material is heated and reaches a temperature of up to 950 °C. By inserting air at the bottom of the reactor and three different levels for secondary air supply, the combustion as well as the discharge rate of the bed material can be controlled. The discharged hot bed material is separated from the flue gas (FG) by a cyclone and fed back into the gasification reactor via a steam-flushed siphon, which serves also as a gas barrier. In this way, the necessary energy is supplied to the gasification process via the bed material.

In addition, the combustion reactor is also used for the disposal or thermal utilization of separated residual materials such as fly char and the separated RME-tar-water emulsion from the product gas. Fresh bed material or additives like limestone are also fed into this part of the reactor system. In order to keep the temperature in the reactor as constant as possible despite these often irregularly supplied energy sources, the recirculation blower, recirculates small quantities of product gas into the CR as required. Heating oil can also be used as an auxiliary fuel in the CR. This is required to heat up the reactor system from 700 °C and to keep the system warm if no fuel is supplied or the product gas recirculation fails.

After bed material separation in the cyclone the hot flue gas (FG) is also cooled by a thermal radiation cooler like the one at the PG path. The following cyclone separates the fly ash from the gas stream and passes the gas to an air heater, which is designed as a shell-and-tube heat exchanger. The thermal energy of the exhaust gas (400–550 °C) is used to preheat the process air for the combustion process. After the heat exchanger, a water-cooled redundant cooler is used to lower the temperature of the gas, so that the gas can pass the following fabric filter. The filter is also cleaned with nitrogen and the filter cake is disposed of with the ash separated before. After this cleaning process the gas passes two fans and flows partially into the post combustion chamber or directly to the industrial facilities of Wien Energie for further flue gas cleaning.

In the post combustion chamber, a heating oil combustion system, ensures that the PG is burned completely. This prevents potentially dangerous concentrations of flammable gas in the FG flow to the industrial facilities of Wien Energie. Before the FG passes on to the industrial facilities of Wien Energie for flue gas cleaning it passes through a boiler to lower its temperature.

The boiler is connected to a steam drum into which the steam and hot water flows from the radiant coolers and redundant cooler, scrubber media cooling and ash transport line cooling are fed. The heat is released into the environment via cooler fans and the desalinated water used condenses and is fed back into the steam drum. This creates

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a natural circulation of the cooling system. Therefore, most of the thermal energy generated in this plant is not used to increase the efficiency.

3.2 Fuel characteristics

An overview of the fuels used to date in the 1 MW demonstration plant is provided. The fuel properties of the materials differ in the parameters listed below as well as in properties that are not precisely recorded, such as particle size distribution, flowability or segregation properties of the bulk material.

Category 1 wood chips (WC) are clean WC from logs. This fuel is used as a benchmark fuel to enable comparisons with the Güssing, Senden and GoBiGas plants. Category 3 WC include higher proportions of bark and branches and are therefore of poorer quality. WC of category 5 are also referred to as forest residues, and consist mainly of forestry harvest residues such as tree tops, branches, and roots and is therefore the lowest WC quality. The water content increases sharply with decreasing quality, which indicates the different storage locations and storage times. The lower heating value on a dry basis (LHV_{db}) of the three fuels is similar, but the water contents of the fuels have a strong influence on the LHV. An increasing ash content as well as increasing nitrogen, sulfur and chloride contents in the three categories indicate the growing proportions of bark and needles.

The values for the bark fuel are made up of two measurements. Certain fluctuations in the fuel composition are to be expected for both natural fuels and waste streams. The mean value is intended to represent a probable value. Compared to WC, a higher ash content and increased nitrogen and sulfur contents are noticeable. The LHV is only slightly lower.

Wood pellets were used for the analysis of manipulated variables, as they have very uniform properties over the entire period of use. No own analysis was commissioned but the data from the manufacturer was used.

Tests with samples from the paper industry were also carried out. Due to the properties of the fuel rejects, such as high LHV_{db} , high water content and poor flowability, a 1/1 wt.-% mixture of rejects with category 1 WC (Blend WC/R) was used. The resulting calculated parameters are also shown in Table 11. The high chlorine content compared to the other fuels is remarkable.

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<i>Parameter</i>	<i>Unit</i>	<i>WC Cat. 1</i>	<i>WC Cat. 3</i>	<i>WC Cat. 5</i>	<i>Bark</i>	<i>Wood Pellets</i>	<i>Rejects</i>	<i>Blend: WC/R</i>
<i>Moisture</i>	wt.-%	14,3	34,1	50,8	22,3	5,1	57,1	37,1
<i>Ash content</i>	wt.- % _{db}	0,9	2,3	5,6	8,3	0,4	12,5	6,7
<i>Volatiles</i>	wt.- % _{daf}	84,9	80,1	77,3	74,1	-	82	82,9
<i>Carbon</i>	wt.- % _{daf}	49,4	49,9	50,7	49,4	-	58,9	54,2
<i>Hydrogen</i>	wt.- % _{daf}	5,8	5,9	5,5	5,4	-	8,5	7,2
<i>Nitrogen</i>	wt.- % _{daf}	0,1	0,2	0,5	0,55	0,05	0,2	0,2
<i>Sulfur</i>	wt.- % _{daf}	< 0,02	0,03	0,07	0,05	<0,005	0,06	0,03
<i>Chloride</i>	wt.- % _{daf}	< 0,01	< 0,01	0,03	<0,015	<0,005	0,61	0,3
<i>LHV (dry)</i>	MJ/kg	18,4	18,8	18,5	18	-	26,9	22,7
<i>LHV (wet)</i>	MJ/kg	15,4	14,3	7,8	13,5	17,9	10,2	13,5

Table 11: Analyses of feedstocks; average values from two bark analyses; Blend: WC Cat. 1 and plastic rejects mixed 1 wt.-%/1 wt.-%, calculated values

3.3 Sampling

As part of the test campaigns in the plant, samples of the PG were taken at five different measurement points (marked in Figure 14) in the plant and analyzed by an external test laboratory at the Institute of Chemical Engineering from TU Wien called Test Laboratory for Combustion Systems.

Measuring points:

1. PG freeboard gasifier
2. PG after radiation cooler
3. PG after ceramic hot gas filter
4. PG after water quench
5. PG after PG blower

The measurement points were chosen at locations where the measurements can provide important results regarding the reactor design and the subsequent gas cleaning. By measuring in the freeboard of the gasification unit, the gas composition and contamination can be determined before the gas comes into contact with the CCC. After the radiation cooler, the measurement provides information about the changes in the gas via the CCC as well as the particle content after the radiation coolers. As the gas cools down via the radiation cooler to the temperature that also prevails at the ceramic cartridge filter, the measurement after the filter can be used to make statements about the separation at the filter. The further step of water quenching cools the gas down considerably to an average of 35 °C and the water content and the proportion of water-soluble components in the gas decreases significantly. By measuring after the quench, these reductions and the content of tars separated in the scrubber can be determined. By measuring the gas after the PG blower, the reduction of impurities, mainly tar reduction, via the RME scrubber is investigated. It is assumed that the PG blower has no separation effect on impurities in the gas.

The following PG impurities were analyzed: particle content, water content, tar content, H₂S content, NH₃ content, HCl and HF content. When measuring the particle content, a distinction was made between fly char particles and inorganic particles such as ash or bed material, this component of the analysis is further referred to as dust. Not all analyses were carried out for every fuel. An overview of the performed analyses and the number of measurements is presented in each subchapter of chapter 4.

The setup arrangement of the offline sampling system for particle, water and tar content is shown in Figure 15 and Figure 16. This method is based on the official standard CEN/TS 15439 which is based on the tar guideline [20] and was slightly adapted for DFB gasification by using a different solvent. Instead of isopropanol,

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toluene is used as a solvent in order to take into account the comparably high water content resulting from the use of steam as a gasification medium.

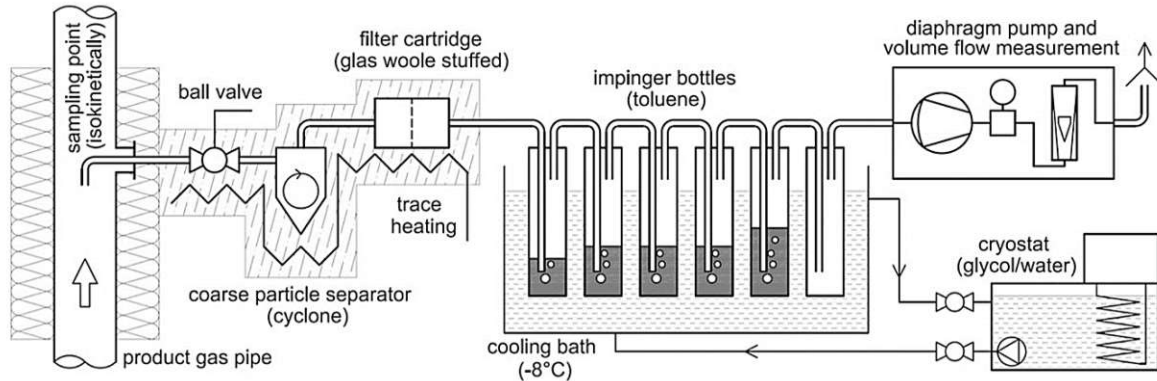


Figure 15: Sampling setup for particle-, water- and tar content [17]

During sampling, a partial flow with a flow rate of 10 l/min of the product gas is drawn off over a measured time and passed through a heated pipe to the particle separator containing a cyclone and filter cartridge filled with glass wool. Char and other particles are separated in this area. At measurement point 5 an additional plane filter head is fitted in front of the apparatus to measure finer particles. After the filter, the gas is passed through five cooled Impinger bottles filled with toluene and one empty bottle, which are cooled to $-8\text{ }^{\circ}\text{C}$ in a cooling bath. Water present in the gas is condensed out in the cylinders and tars are condensed and dissolved. The empty bottle is used for droplet separation upstream of the pump with which the flow rate is adjusted. The measuring time is influenced by the sampling point and is usually between 8 and 30 minutes depending on the contamination of the gas.



Figure 16: Example of the measurement setup at measuring point 3

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The particles from the cyclone are washed into the filter cartridge, and a filtration of the liquid phase is required to collect all the particles and prevent a contamination of the liquid phase. The cartridge and filter are dried at 105 °C and 6 h and are weighted afterwards. To extract tars from the particles, the dry particles are brought into contact with isopropanol. The cleaned particles are dried, weighted and incinerated to determine the dust and fly char share. The amount of extracted solution is registered and a sample is used for GC/MS analyses. The toluene solvent of the Impinger bottles get collected and a separation of water phase from organic solvent can be done. This enables volumetric determination of the water content in the PG. The amount of toluene solution is registered and a sample for GC/MS analyses is taken before the solution gets evaporated in three steps. Firstly, rotary evaporation at 60 °C and 80 mbar, Secondly, evaporation at atmospheric ambient for 12 h and finally, evaporation for 6 h at 105 °C in a drier. By weighing the residues part of the gravimetric tars can be determined. The previously taken samples as well as the solution from the particle preparation and the remaining previously separated phases are also processed according to the three steps and the residues result in the remaining gravimetric tars.

The measurement setup for H₂S and NH₃ differs only in the temperature of the cooling (2 °C) and the washing liquid used in the Impinger bottles. For H₂S the adsorption solution KOH 35% is used in the second and third bottle while toluene is used for tar separation in the first bottle and as droplet separator in the fourth bottle. The flow rate is about three liters per minute. The samples are separated again and the H₂S content is determined by potentiometric titration. For NH₃ sampling the first three bottles are filled with 0.05 mol/L H₂SO₄ and the following bottles are prepared as droplet and tar separators to protect the pump. The solution is then analyzed by ion chromatography.

A more detailed description of the analytic processes is given by Wolfesberger-Schwabl. [17]

4 Results

It is important to mention that the evaluation of the data presented in the frame of the thesis only relates to gas cleaning. Different operating conditions of the DFB gasifier provide different gas compositions as well as different contents of impurities in the gas. Figure 17 is shown as an illustrative example for tar content of gas from high quality WC (category 1) on different days and operating conditions.

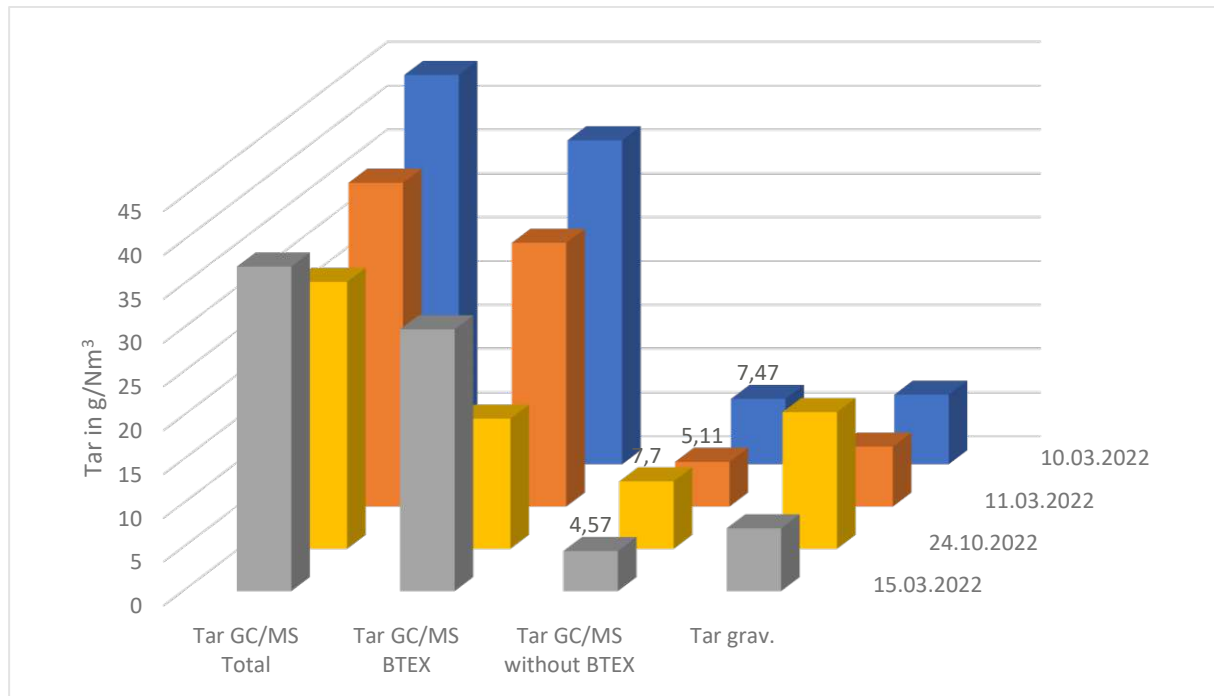


Figure 17: Tar content after radiation cooler over different gasifier operation conditions with WC Category 1

If several measurements per impurity and stage were carried out for one fuel, these were averaged in the evaluation in order to be able to compare the results with other fuels.

4.1 Water content and separation

Table 12 shows the number of water measurements taken at the different gas cleaning measurement points. The water measurements were carried out in the course of the tar measurements. The data in the Figure 18 show the mean values and standard deviation for WC Cat. 1 and bark with standard deviation for points with three or more measurements, as well as the individual measured values for the other fuels.

Measurement point:	1	2	3	4	5
WC Cat.1	5	5	3	3	6
WC Cat.3	0	1	1	1	1
WC Cat.5	1	1	0	0	0
Bark	3	3	2	2	3
Pellets	0	0	0	0	0
Blend: WC/R	1	1	1	1	1

Table 12: Number of water content measurements for different feedstocks

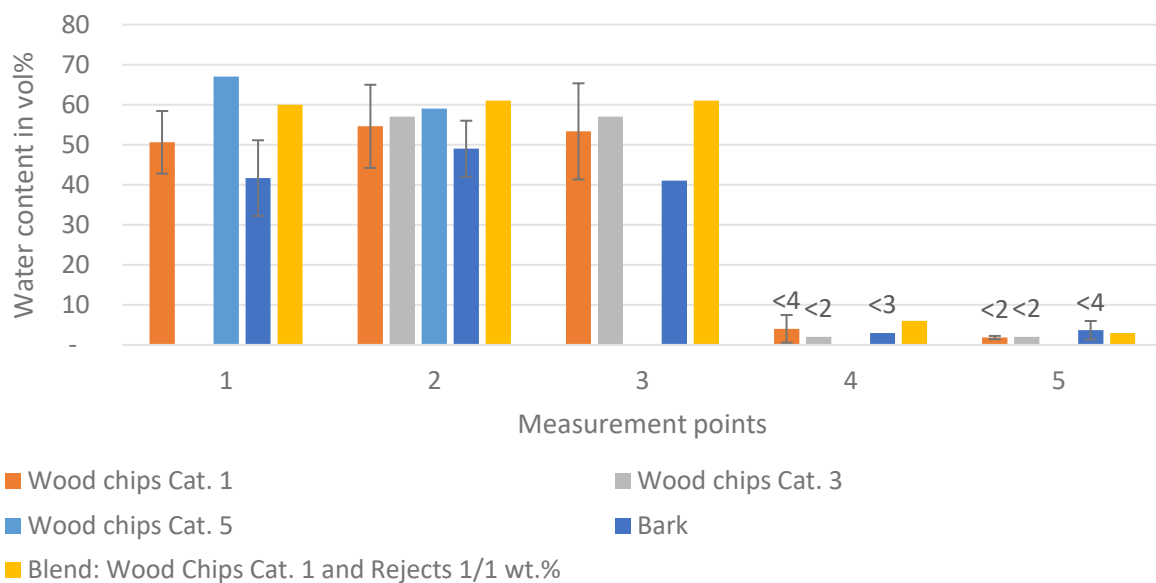


Figure 18: Average PG water content for different feedstocks; MP 4 and MP 5: average values for WC Cat. 1, Cat. 3 and bark are lower than calculated, due to not detected true values smaller than analyzed values

For WC Cat. 5 at the measurement point (MP) 1 and 2 and the wood chip/reject mixture at the MP 1 to 4 a slightly higher water contents in comparison to the other fuels can be seen. Significantly reduced water contents were measured at MP 4, which results from the condensation in the water scrubber. Figure 19 shows the total water separation efficiency of the PG path, calculated with the average water content from Figure 18. Over the MP 1–3, small fluctuations in the water content are shown that can lie within the measurement uncertainty of the analysis. The water quench reaches a water content reduction of over 90% compared to the initial value at MP 1 of all

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feedstocks. For feedstock WC Cat. 1 and the WC reject blend a small reduction of water content can also be measured from MP 4 to MP 5, which represents the RME-scrubber. Due to the not exactly determined water contents in MP 4 and 5, a higher separation rate can also occur here.

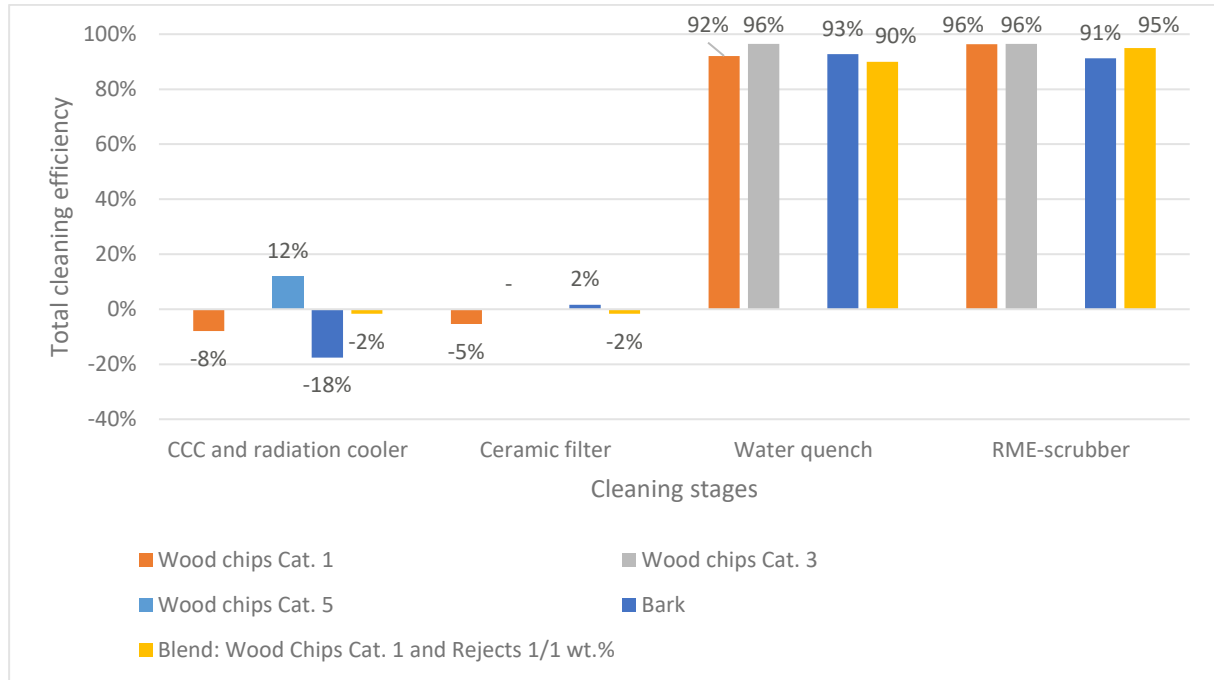


Figure 19: Average total separation efficiency for water of the gas cleaning path

4.2 Particle content and separation

In the course of particle measurements, a subdivision into dust and fly char is undertaken. No differentiation of the measured particles is made in the planar filter measurements at MP 5. The number of taken measurements can be found in Table 13. One measurement of WC Cat. 1 at MP 5 was not included in the evaluation for reasons of plausibility.

Dust:						Fly char:					
Measurement point:	1	2	3	4	5	Measurement point:	1	2	3	4	5
WC Cat. 1	5	4	3	1	(4)	WC Cat. 1	5	5	3	1	0
WC Cat. 3	1	1	1	1	0	WC Cat. 3	1	1	1	1	0
WC Cat. 5	1	1	0	0	0	WC Cat. 5	1	1	0	0	0
Bark	3	3	2	2	0	Bark	3	2	2	2	0
Pellets	0	0	0	0	0	Pellets	0	0	0	0	0
Blend: WC/R	1	1	1	1	(1)	Blend: WC/R	1	1	1	1	0

Table 13: Number of particle measurements for different feedstocks. Measurements at MP 5 were conducted with planar filter and are not divided in dust and fly char

Figure 20 and Figure 21 show the particle concentration for the gas cleaning path. It is noticeable that bark and the WC/R mixture have high initial dust concentrations compared to the other fuels. Only in the case of bark can this also be observed for fly ash. However, the dust concentration of the mixture decreases faster than that of the bark during gas cleaning. In general, it can be observed that the dust decreases more than the fly ash via the ceramic cartridge filter (between MP 2 and 3).

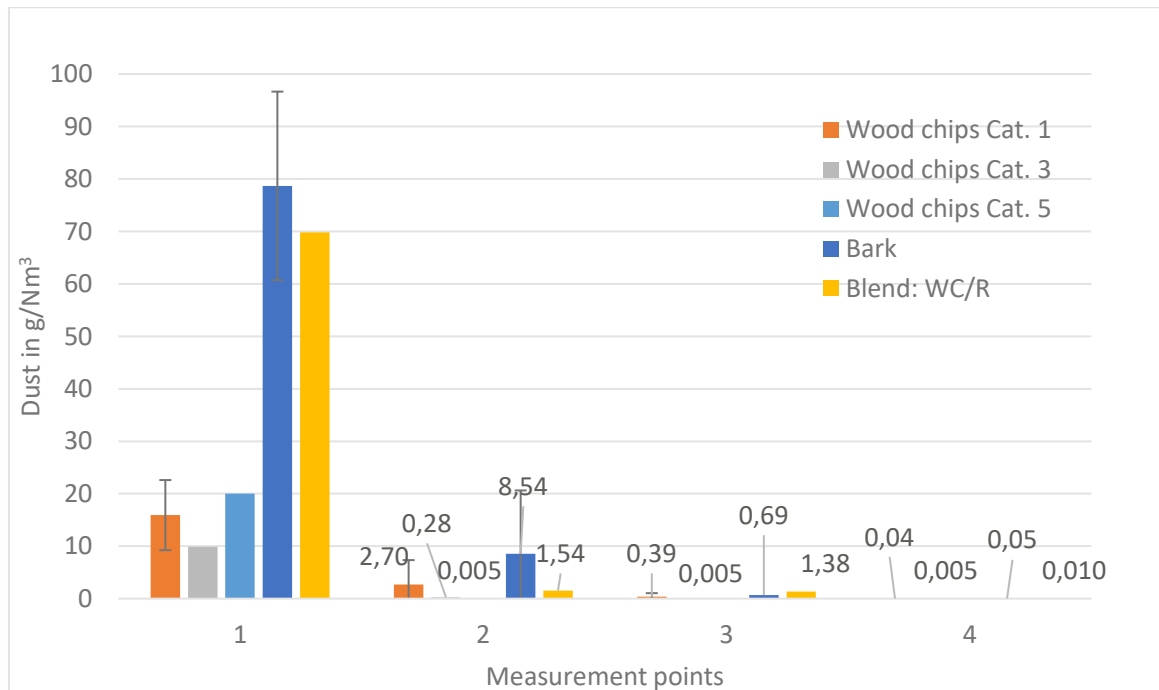


Figure 20: Dust particle concentration of measurement point 1 to 4 in g/Nm³

Results

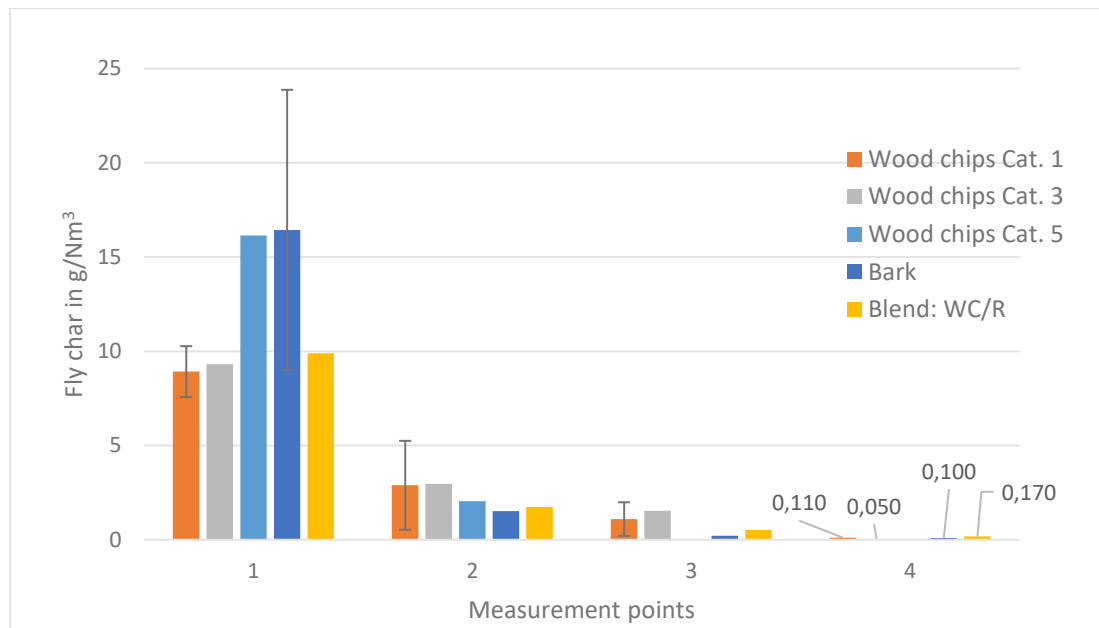


Figure 21: fly char particle concentration of measurement points 1 to 4 in g/Nm^3

Figure 22 at MP 4 and 5, the concentration is given in mg/Nm^3 as the concentrations and the limit values for further use in gas engines and syntheses are low. None of the fuels reaches the limit value of the gas engine before the RME scrubber (no measurement data for WC Cat. 5). The measurements on MP 5 after the RME scrubber for WC Cat. 1 and WC/R show that the limit value for the gas engine is reached. For the further upgrading of the products gas via syntheses processes further fine gas cleaning would be necessary.

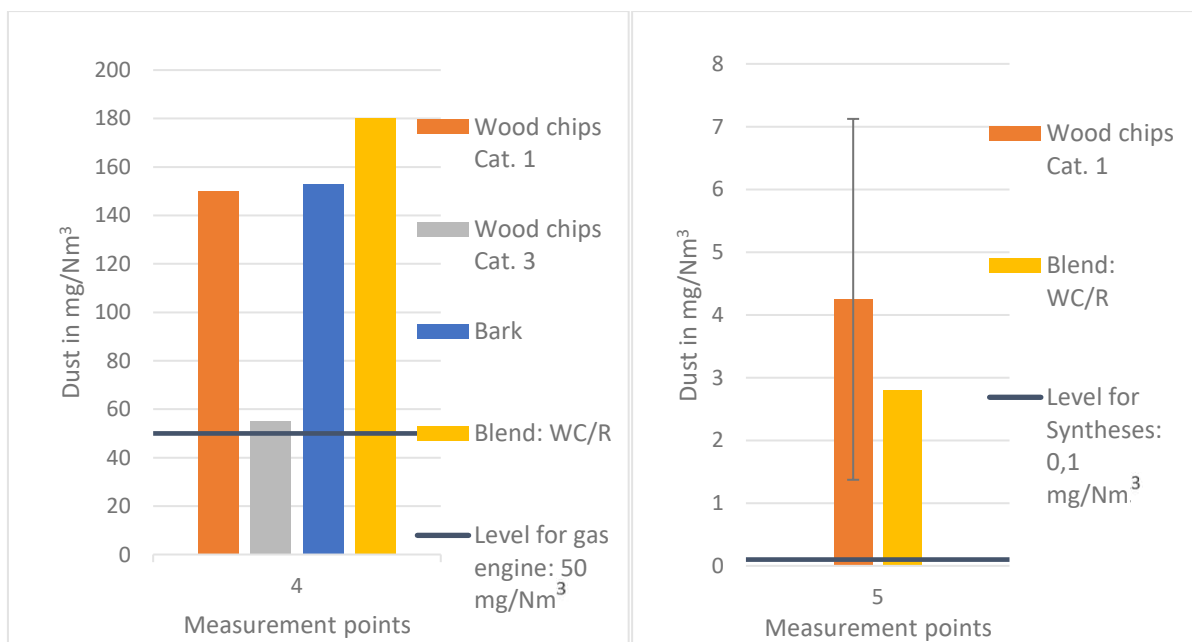


Figure 22: Dust particle concentration of measurement point 4 and 5 in mg/Nm^3 , measurement method with planar filter in point 5; marked level for utilization in gas engine or synthesis

4.3 NH₃ content and separation

The collective representation of the NH₃ measurements is shown in Table 14.

Measurement point:	1	2	3	4	5
WC Cat. 1	1	4	1	2	4
WC Cat. 3	0	1	0	1	0
WC Cat. 5	0	0	0	0	1
Bark	1	0	1	3	1
Pellets	0	0	1	1	1
Blend: WC/R	0	1	0	1	2

Table 14: Number of particle measurements for different feedstocks

Due to irregularly distributed measurements and varying operating modes during the test campaigns, the change in NH₃ concentration over the PG can only be described with initial observations and no final statements can be made. The measurement result of 1088 ppm for WC Cat. 5 at MP 5 was not used for further calculations, as there are no comparative measurements for this fuel. For WC Cat. 1, from four measurements at MP 2 a mean value of 806 ppm with a standard deviation of 550 ppm was calculated. Four measurements at MP 5 deliver a mean value of 22,3 ppm with a standard deviation of 36,5 ppm.

High NH₃ concentrations in the bark fuel as well as the value of WC Cat. 5 (MP 5) compared to the other fuels can be seen in Figure 23. The reduction of the NH₃ content can be observed via the PG cleaning section for WC Cat. 3, pellets and WC/R. For WC Cat. 1 and bark, an increase can be seen between MP1 and MP 2/MP 3. An increase in the concentration of bark from MP 4 to MP 5 over the RME-scrubber can also be observed. All bark measurements at MP 4 are below 601 ppm, compared to 901 ppm at MP 5.

Results

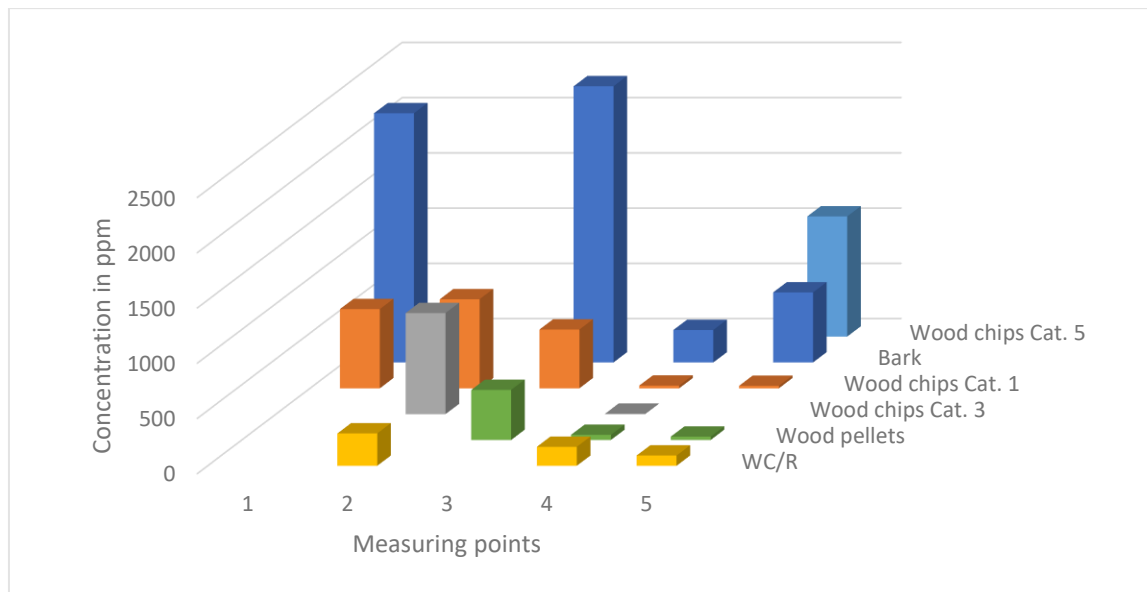


Figure 23: First results of NH₃ content over the PG cleaning path

Figure 24 shows the calculated overall reduction in NH₃ concentration across the PG cleaning stages. Due to the fluctuating measurements, only initial reference values can be given. The water quench shows high removal rates of over 90% for the fuels WC Cat. 3, bark and pellets, while lower reductions are measured for WC Cat. 1 and WC/R. For bark and the WC/R mixture, the overall reduction lies around 70%.

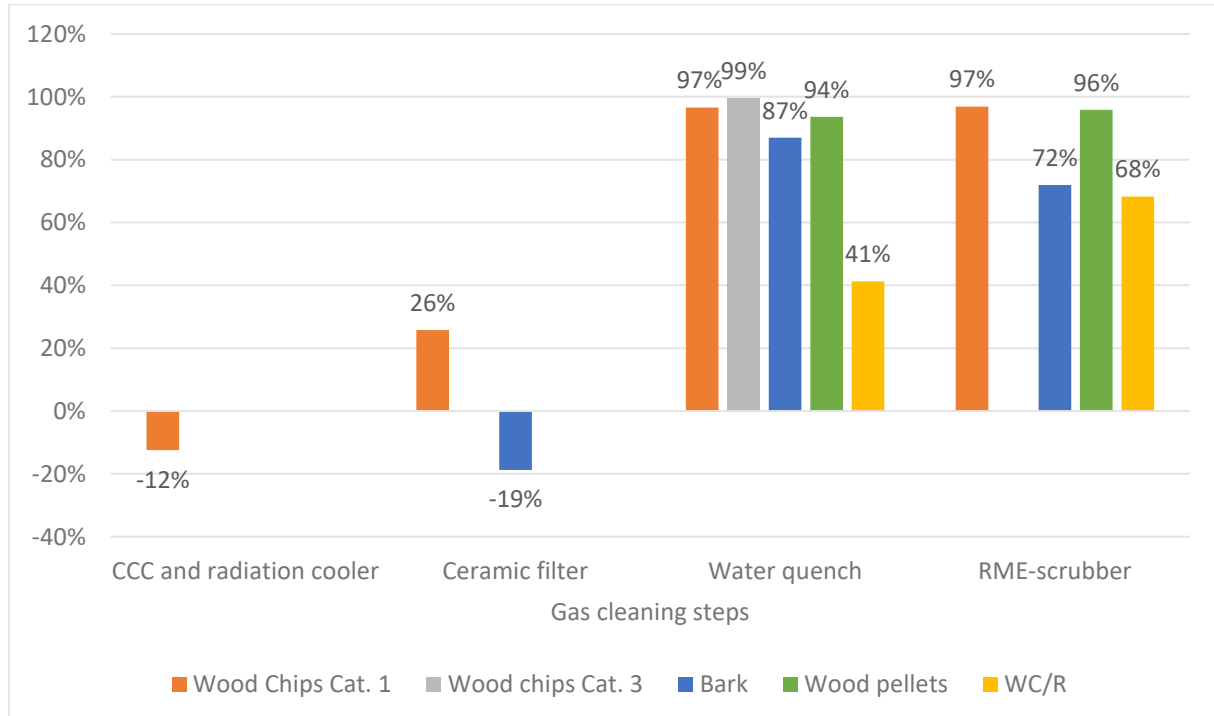


Figure 24: First calculation values for total separation efficiency of the PG cleaning path

4.4 Tar content and separation

The following graphs show the results of the tar analyses counted in Table 15.

Measurement point:	1	2	3	4	5
WC Cat.1	5	5	3	3	6
WC Cat.3	1	1	1	1	1
WC Cat.5	1	1	0	0	0
Bark	3	3	2	2	3
Pellets	0	0	0	0	0
Blend: WC/R	1	1	1	1	1

Table 15: Number of tar measurements for different feedstocks

Usually, the value of the GC/MS tar without BTEX is considered for the evaluation of the gasification operation [17]. However, due to the importance of BTEX in the possible downstream applications, the GC/MS BTEX component is also shown in the following evaluations.

Since several measurements have already been carried out for the fuel WC Cat. 1 on different days, Figure 25 shows an exemplarily measurement campaign from 11.3.2022. It is noticeable that all tar compounds except GC/MS tar without BTEX decrease over the PG cleaning path. For GC/MS tar without BTEX a slight increase at MP 3 compared with MP 2 can be observed. Nevertheless, if all measurements from different campaigns for the fuel are averaged, a reduction is also seen for the GC/MS tar without BTEX value shown in Figure 26.

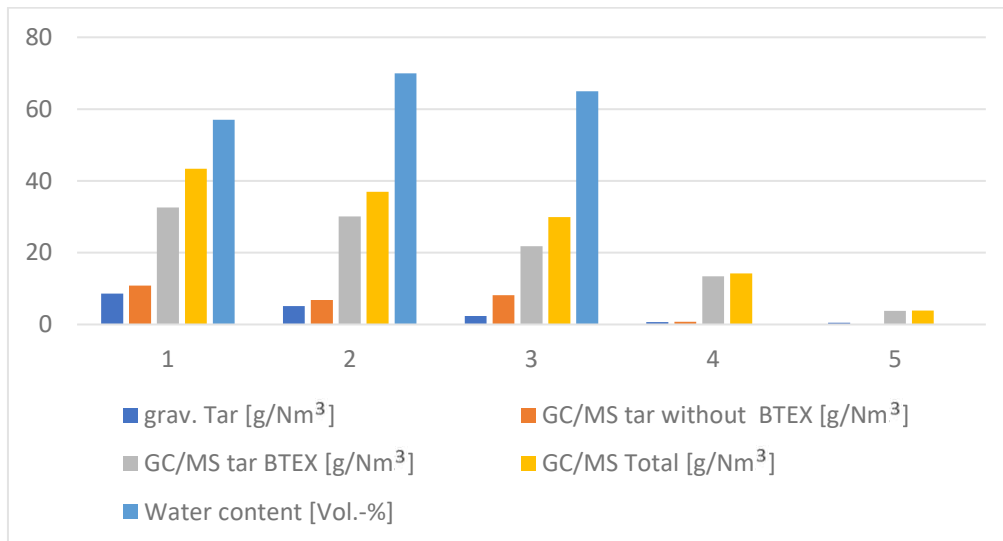


Figure 25: Tar measurement results from 11.3.2022 for the fuel WC Cat. 1

Results

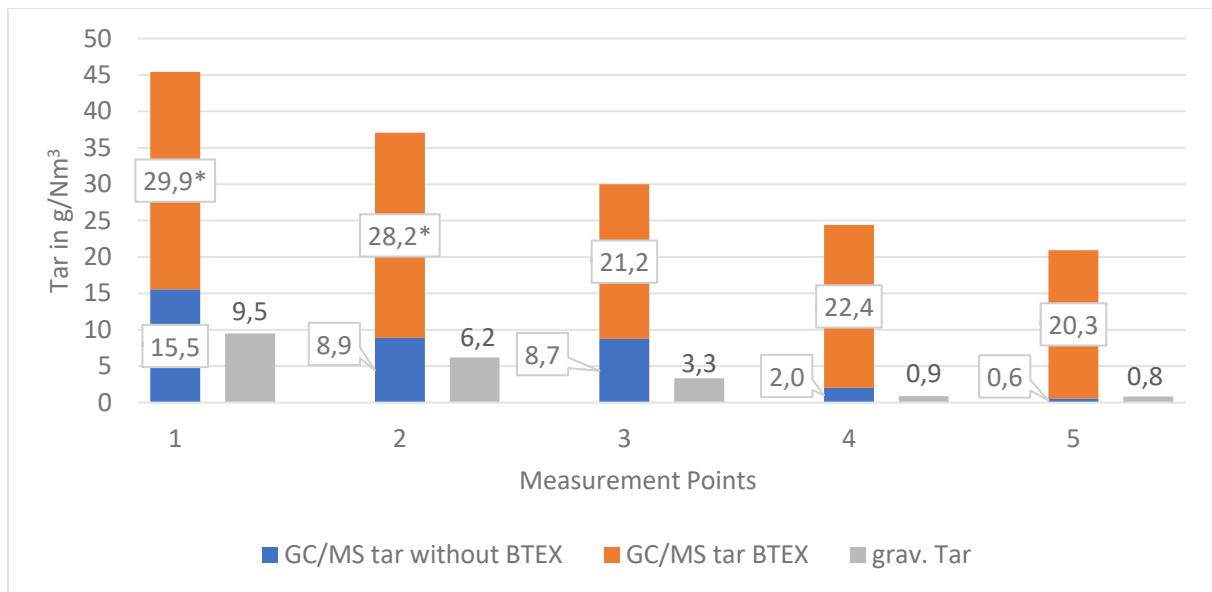


Figure 26: Tar measurement for feedstock WC Cat. 1; with * marked values were calculated with data that was not determined exactly but whose true value is higher than the stated analysis result

In Figure 26 - Figure 30 the behavior of tars for different fuels over the PG path are given.

As with WC Cat. 1, for all feedstocks a reduction of the GC/MS tar without BTEX, GC/MS BTEX tar and the gravimetric tar from MP 1 to MP 5 is recognizable.

When comparing the fuels at MP 1, bark is the fuel with the highest GC/MS tar without BTEX content, the mixture WC/R with the highest GC/MS BTEX tar content and WC Cat. 5 with the highest gravimetric tar content.

For WC Cat. 3, bark and the mixture WC/R, slight increases in GC/MS tar without BTEX at MP 3 are recognizable. The rest of the components are reduced.

The lowest values at MP 5 are detected for the blend WC/R, whereby the GC/MS BTEX values are not counted as they may be higher than the specified value.

Results

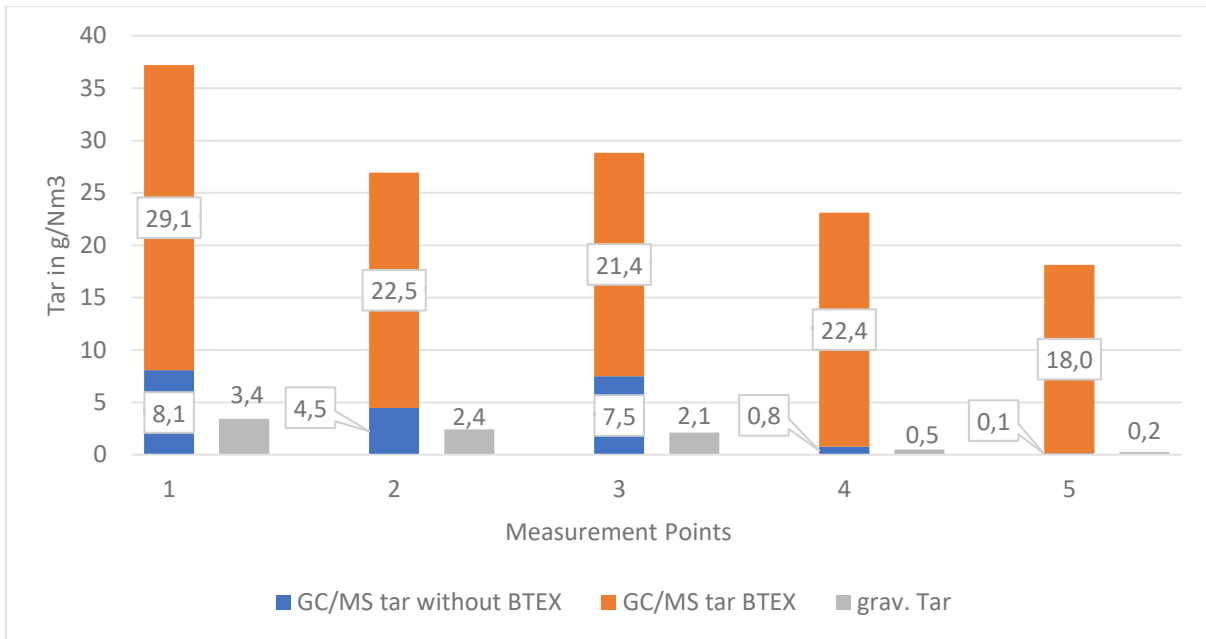


Figure 27: Tar measurement for feedstock WC Cat. 3

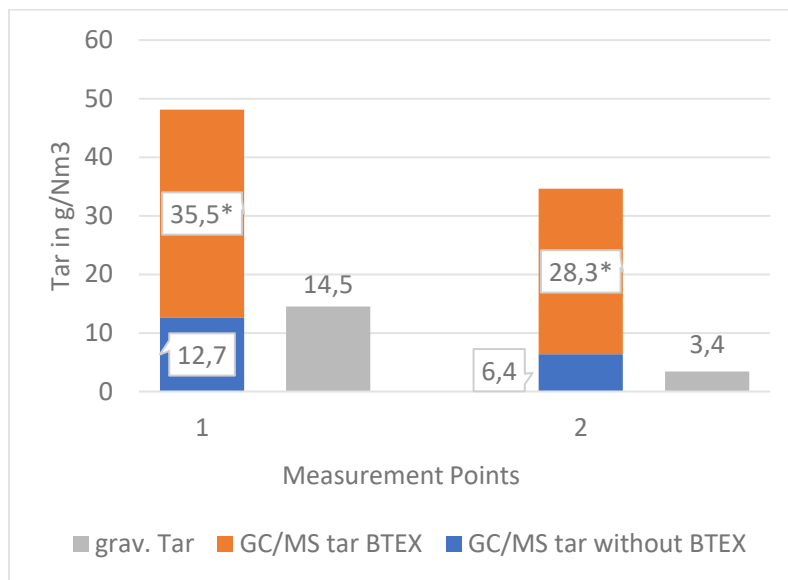


Figure 28: Tar measurement for feedstock WC Cat. 5; with * marked values were calculated with data that was not determined exactly but whose true value is higher than the stated analysis result

Results

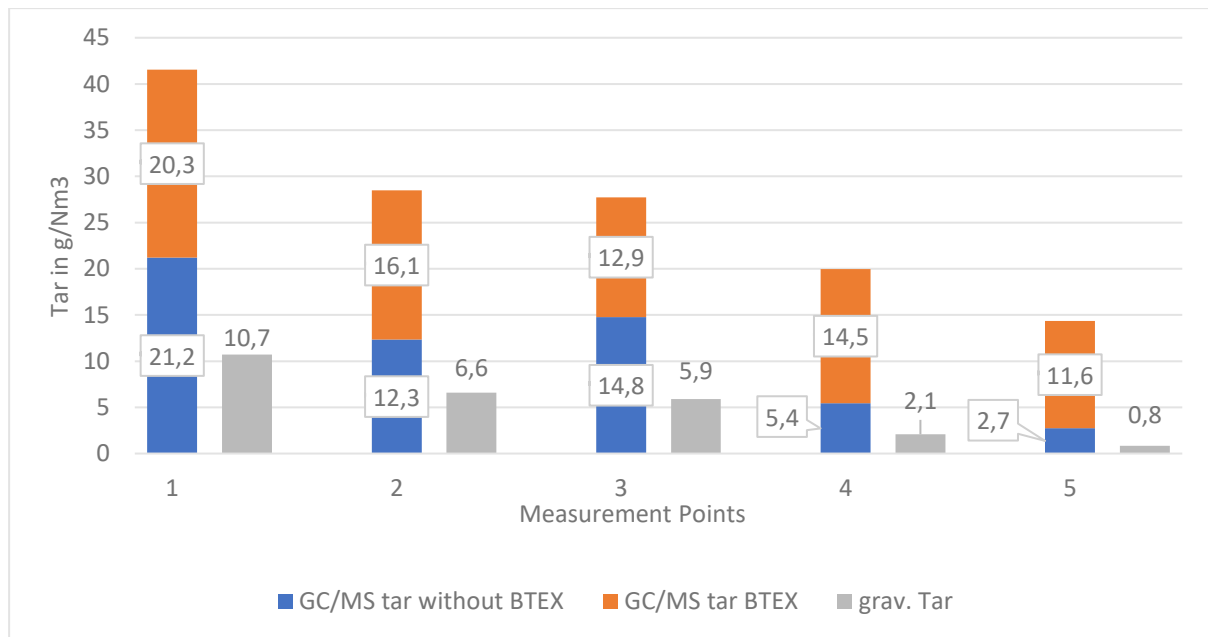


Figure 29: Tar measurement for feedstock bark

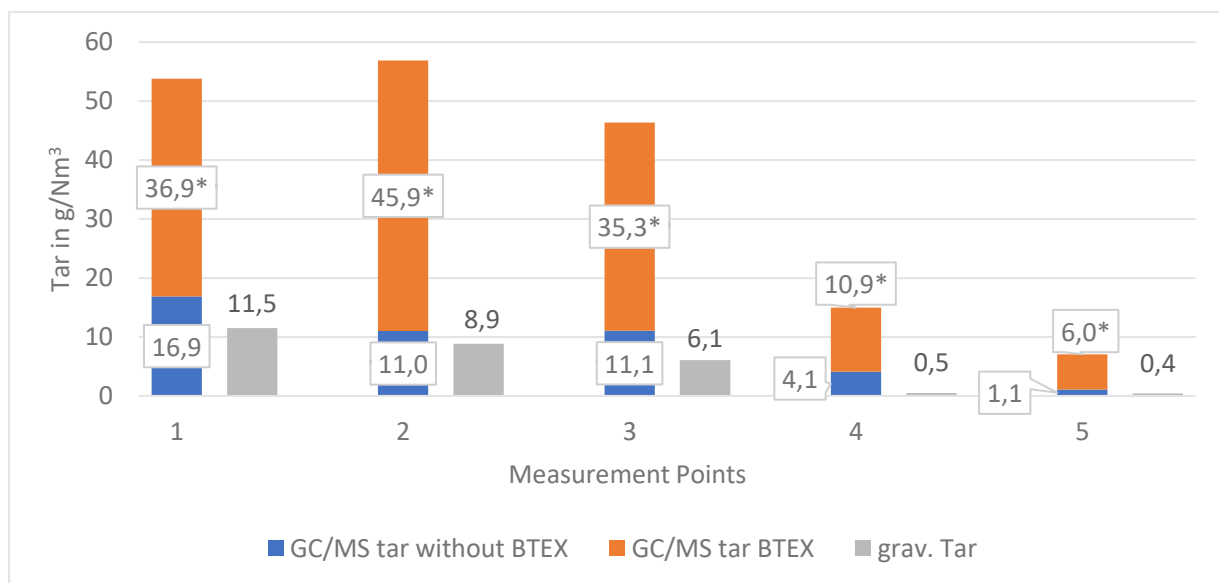


Figure 30: Tar measurement for WC/R blend; with * marked values were calculated with data that was not determined exactly but whose true value is higher than the stated analysis result

Figure 31 shows the calculated separation of GC/MS tar without BTEX via the product gas cleaning section mainly takes place via the CCC as well as via the water quench and the RME scrubber. Separation rates via the CCC are between 50% for WC Cat. 5 and 35% for WC/R. A decreasing separation rate via the ceramic cartridge filter is due to the already mentioned higher concentrations at MP 3 compared to MP 2. 40% or more of these tars are again separated in the water quench and a finer cleaning to a total separation efficiency of up to 98% for WC Cat. 3 takes place via the RME scrubber.

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Very similar deposition rates can also be achieved with gravimetric tar see Figure 33. A total separation rate of over 90% can be achieved for all fuels (unknown for WC Cat. 5).

Looking at the separation of the GC/MS BTEX tars (Figure 32), separation rates of up to a maximum of 52% are achieved for WC and bark. Since the analysis results of the measurements for WC/R are only delimited downwards (content in the sample greater than the specified value), no statement can be made for the exact separation rate. The calculated values for the WC/R mixture reach up to 89%, but must be regarded as highly unlikely to be achieved.

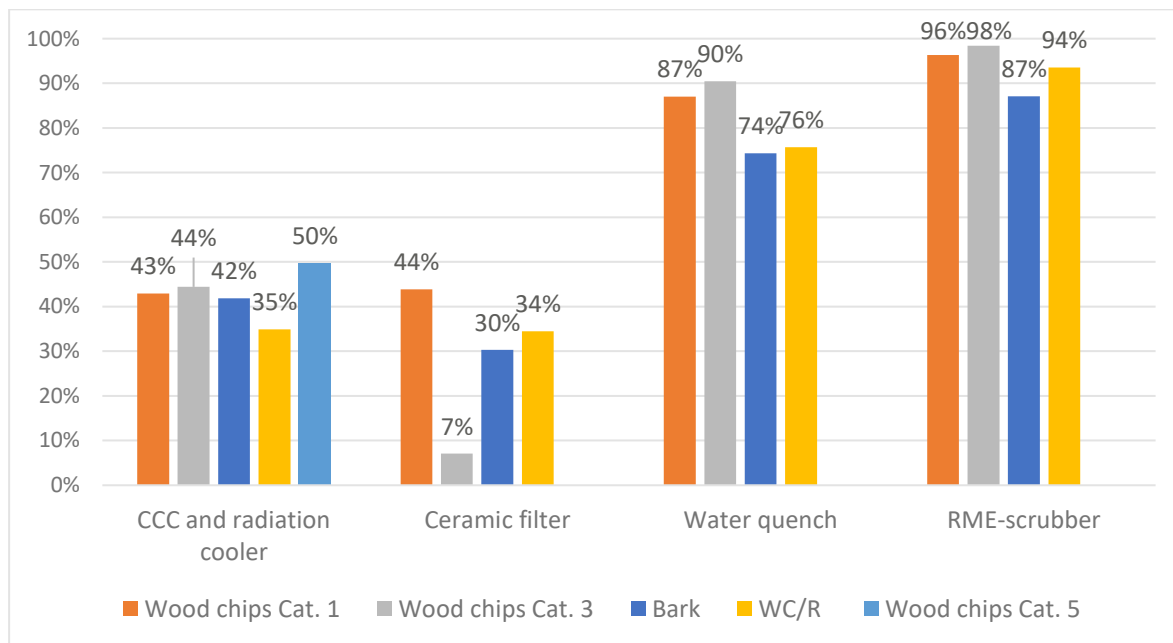


Figure 31: Calculated reduction of GC/MS tar without BTEX for different feedstocks over the PG cleaning path

Results

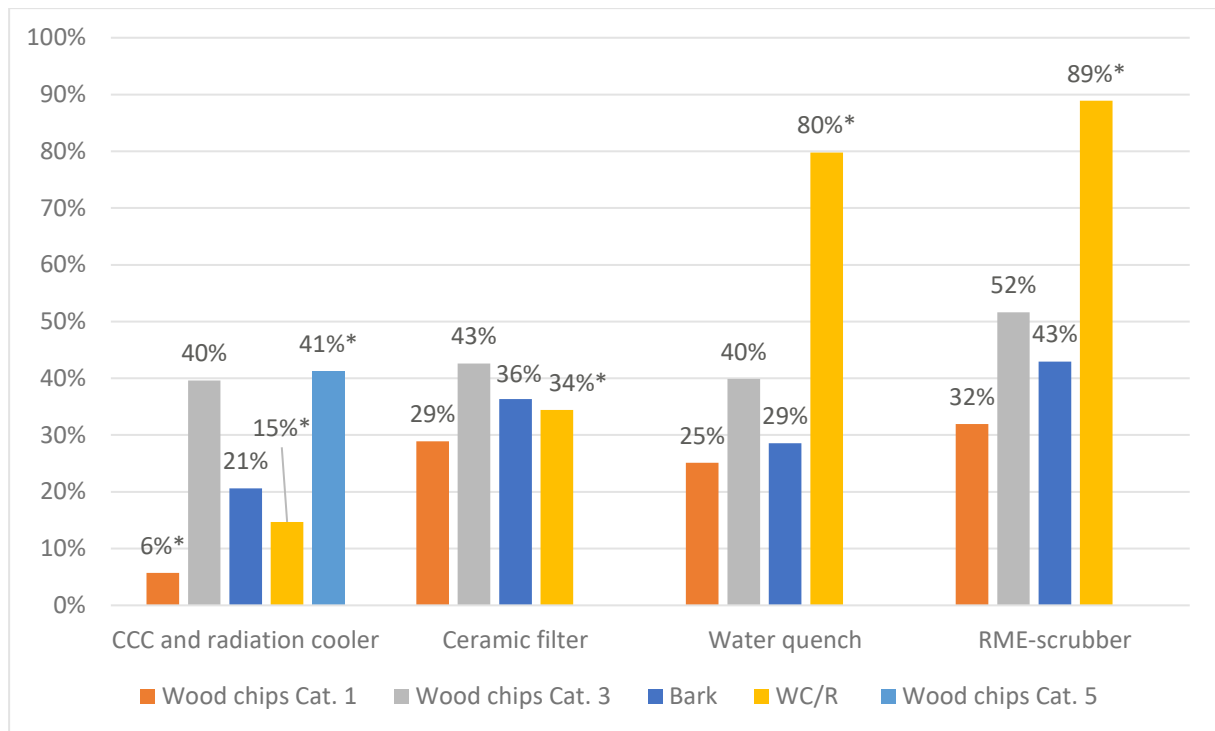


Figure 32: Calculated reduction of GC/MS BTEX tar for different feedstocks over the PG cleaning path; with * marked values were calculated with data that was not determined exactly but whose true value is higher than the stated analysis result, the calculated value would therefore be lower

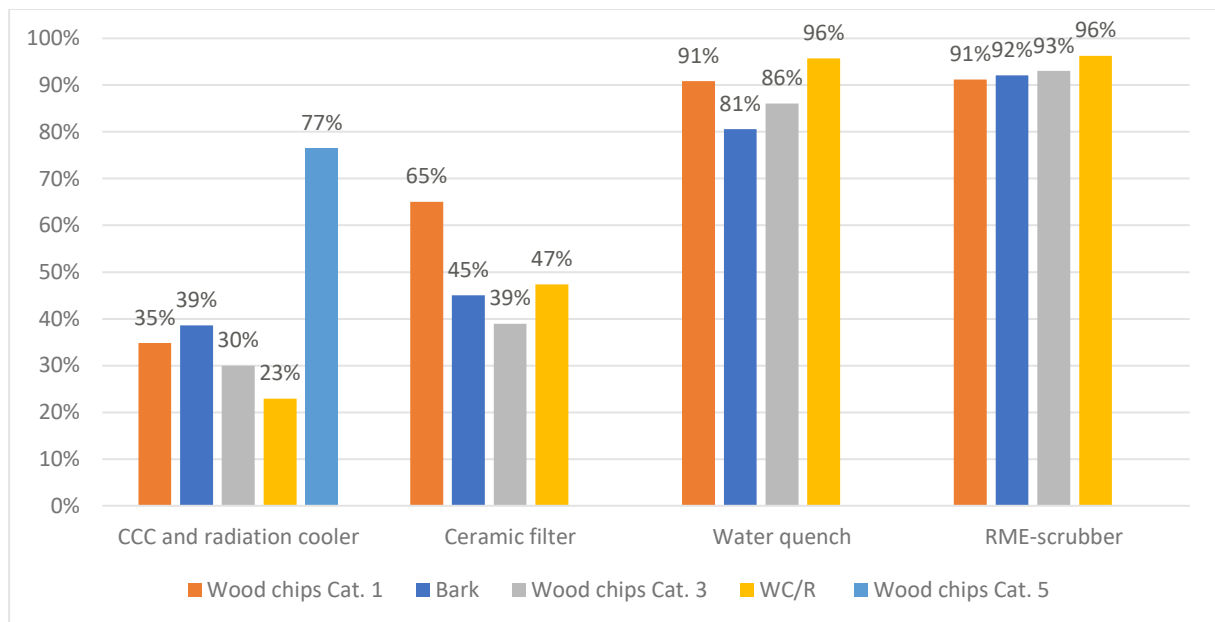


Figure 33: Calculated reduction of gravimetric tar for different feedstocks over the PG cleaning path

4.5 H₂S content

Table 16 shows the number of H₂S measurements carried out to date and provides information on the resulting low data density for the fuels. This means that only previous observations can be reported and no final statements can be made about the behavior of H₂S over the gas path.

Measurement point:	1	2	3	4	5
WC Cat.1	1	3	1	2	3
WC Cat.3	0	1	0	1	0
Bark	1	0	0	2	1
Blend: WC/R	0	1	0	1	1

Table 16: Number of H₂S measurements for different feedstocks

The H₂S concentrations between the MP are subject to fluctuations in some cases shown in Figure 34. Due to incomplete measurement series, it is difficult to draw comparisons between the fuels. A reduction in the H₂S content via the PG path is shown by the results of WC Cat. 1. For WC Cat. 1 at MP 1 a mean value of 122 ppm with a standard deviation of 77 ppm was calculated and at MP 5 a mean value of 57 ppm with 33 ppm standard deviation. The measurements of WC Cat. 1 and WC/R at MP 4 and 5 indicate an increase in the concentration via the RME scrubbing.

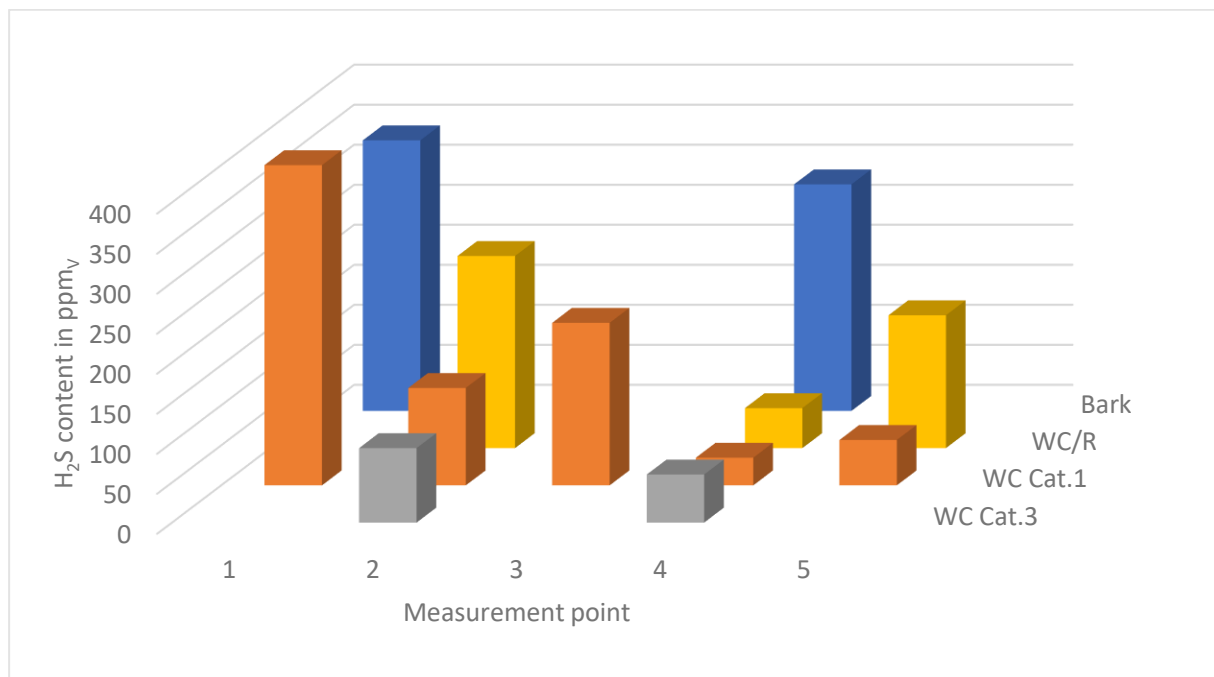


Figure 34: H₂S concentration of different feedstocks over the PG cleaning path

4.6 HCl content

HCl measurements were carried out for WC Cat. 1 and the mixture WC/R. Only the mixture WC/R showed HCl above the limit of quantification (see Figure 35). Due to the limited data available, only an initial statement can be made about the separation of HCl via the PG cleaning path. The separation via filter, scrubber and RME scrubber resulted in a final concentration of 1 ppmv (1,52 mg/Nm³) which is below the limit for gas engines of 500 mg/Nm³ and above the limit for syntheses of 0,01 ppmv. This results in a separation rate of 97%.

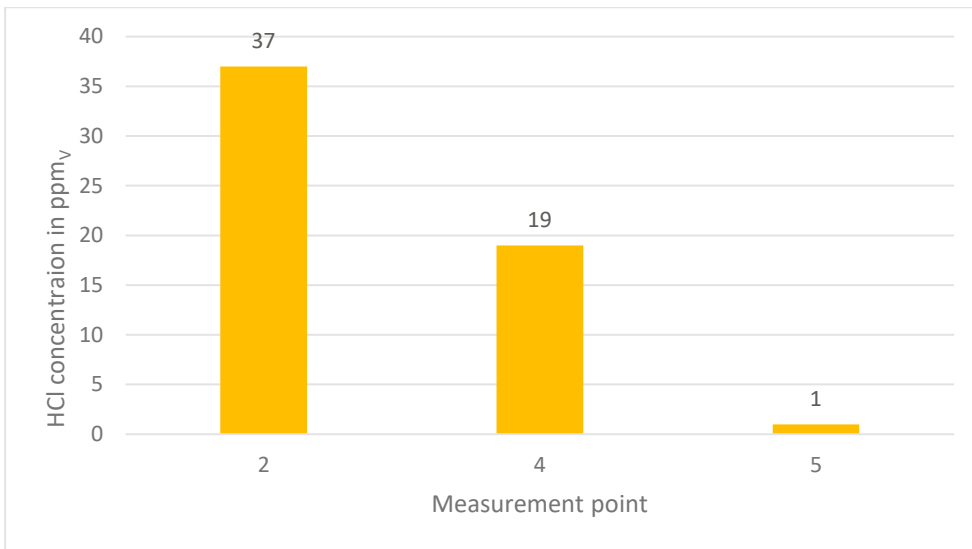


Figure 35: HCl Content of WC/R blend over the PG cleaning path

5 Discussion

Due to the selection of category 1 WC as the reference fuel, there are significantly more measurements for this fuel via the PG path in comparison to other fuels used during 1 MW demonstration campaigns. This means that the average water-, particle- and tar content after the product cleaning can already be compared with the average values after PG cleaning from the plants with the conventional reactor design and the gas cleaning with cooling, filtering and RME washing. An order-of-magnitude classification can be made for components that are not yet measured so frequently as well as for results of other fuels.

Typical data of product gas from WC from the conventional reactor design and cold gas cleaning system is shown in Table 17:

	<i>Unit</i>	<i>Mean value</i>	<i>Typical min.</i>	<i>Typical max.</i>
<i>Water content</i>	vol%	8	5	12
<i>Dust particles</i>	mg/Nm ³ _{db}	10	5	20
<i>Char particles</i>	mg/Nm ³ _{db}	8	3	15
<i>Grav. Tar</i>	mg/Nm ³ _{db}	140	50	300
<i>GC-MS tar without BTEX</i>	mg/Nm ³ _{db}	2100	330	4600
<i>NH₃</i>	ppmv	950	500	1800
<i>H₂S</i>	ppmv	60	20	190
<i>HCl</i>	ppmv	2	0,2	7

Table 17: Typical data of product gas components from DFB gasification after cold gas cleaning, [49]

The water content of the PG depends on the operation of the gasifier and the amount of steam introduced as well as the water content of the fuel. A slightly higher water content of WC Cat. 5 and the mixture WC/R compared to the other fuels results in a higher water content in the PG at MP 1-3. The condensation of water in the quench and RME scrubber leads to water contents below the typical minimum of 5 vol% from Table 17 for all fuels and thus to an improvement in separation compared to the conventional set up. The injection of the cooling water and the condensation of the water in the quench also has positive effects on the separation of water-soluble components (e.g. NH₃) and washed out or condensed other components (particles and tars).

The particulate content of the gas decreases significantly from MP 1 to MP 2 compared to the other stages. This is due to the different flow velocities in the reactor and radiation cooler sections. After the CCC, the reactor diameter increases and the gas velocity decreases, while the diameter of the discharged particles also decreases. The same effect also occurs when the gas flow is diverted in the radiation cooler, which acts as a gravity separator in this sector. The higher proportion of particles in bark and WC/R compared to the other fuels may be due to the particle size distribution in the fuel. Especially with bark, there was a higher fine fraction in the fuel, which became

Discussion

apparent during handling it. Reasons for this behavior with the fuel WC/R cannot be given. If the values at MP 5 are compared with the values from Table 17, the average value of WC Cat. 1 is below the minimum values of the conventional setup. Despite the limited data available at MP 5 for the remaining fuels, values in this size range are also expected, as particle separation by absorption is common practice.

A precise observation and comparison of the behavior of NH_3 over the PG cleaning route is difficult, as different results and numbers of samples are available. Typical NH_3 concentration from the conventional gasifier reactor design for WC Cat. 1 after cooler, filter and RME scrubber varied between 500-1800 ppm [49]. These values were achieved with all fuels and were even undercut with WC Cat. 1 and 3 as well as wood pellets and WC/R. WC Cat. 1 as the only fuel with data for each MP allows an estimation of the behavior, whereby MP 1, 2 and 4 with only one or two measured values each cannot be weighted in the same way as MP 2 and 5 with four measurements each. An increase in the NH_3 concentration via the CCC is against the expected development of NH_3 , as Corella et al. [61] showed a reduction in the NH_3 content when using olivine in tests with catalytic materials. This development can also be seen with the fuel bark between MP 1 and 3. Further measurements must be made in order to be able to use average values for further investigation. A reduction in concentration is observed for all fuels except bark during residual gas cleaning. As expected, the separation of the largest proportion occurs in the water quench, where a certain separation performance can already be expected due to condensation of the water from the gas, which is increased by the water scrubbing. The comparatively low separation rate of bark and WC/R at the scrubbing stage must be investigated further due to the data available before statements can be made. The increasing NH_3 concentration via the RME scrubber for the bark fuel also still needs to be investigated. In general, the amount of nitrogen compounds in the PG after gasification relies on the bound nitrogen content of the fuel.

A detailed analysis of the tar behavior and the reduction and increase of different tar species and tar classes over the CCC for the fuels WC Cat. 1 and 5, bark and WC/R has already been undertaken by Huber et. al. [24] and compared with the 100 kW plant at TU Vienna. The data evaluation carried out in this work in relation to the classification by sample analysis should provide an overview of the tar behavior over the product gas cleaning route. Comparable separation efficiencies of the entire product gas line for the different fuels (unknown for WC/R) were found. The results of the WC Cat. 1 achieve a final concentration for GC/MS tar without BTEX of 600 mg/Nm^3 which is at the lower end of the values of the Table 17. The grav. tar is with 840 mg/Nm^3 above the maximum limit. A possible explanation for this result could be a non-optimized RME scrubber operation. Due to technical problems with the RME exchange, too little fresh RME was added to the RME circuit during some of the campaigns. The saturation of

Discussion

the RME used was only subsequently investigated and a low residual solubility of naphthalene. The naphthalene solubility is often used as a control for RME saturation.

Also, for some fuels, an increase in GC/MS tar values without BTEX was also detected via the filter. One possible reason could be catalytic conversion processes at the hot gas filter. This phenomenon has not yet been described in publications and should be investigated in more detail in the future.

The further evaluation for H₂S, HCl and HF cannot be analyzed more precisely due to the limited data available. The measurements of H₂S via the gas purification section reveal fluctuations between the measuring points. As no measurements were taken for COS, it is assumed that a partial conversion to COS via the CCC appears. The HCl concentration of 1 ppm of the WC/R blend after the RME scrubber is still too high for use in synthesis plants and must be lowered in subsequent fine gas cleaning steps for such use.

6 Conclusion and Outlook

Due to the selection of increasingly complex fuels to be investigated and demonstrated in this demonstration plant, product gas cleaning is also confronted with increasing concentrations and complexity of impurities. This analysis was the first to collect the measurement results of the PG path from past campaigns for the tested fuels. However, due to the low data density for impurities beside tar for WC Cat. 1 the significance of the calculated results of this analysis is low and must be checked and further developed with additional and comparative measurements for the gas cleaning path.

To gain a deeper insight of nitrogen and sulfur components it will be necessary to undertake targeted measurement campaigns over the PG cleaning path. In order to make further statements on sulfur separation via gas cleaning, it will be important to take also a closer look at sulfur components beside H_2S . COS or thiophene contents over the PG cleaning path could develop along with the fluctuations in H_2S and explain these fluctuations wherever a conversion or separation of H_2S takes place. NH_3 measurements via the counterflow column and the hot gas filter should be used to obtain data to confirm or refute the trends shown so far. HCN measurements could also provide more information about the development of the N_2 components and the conversion to N_2 .

In the previous measurement campaigns and data analysis, a focus was laid on tar measurements. The tar data analysis shown in Chapter 4 is limited to the evaluation of the tars classified by measurement. The evaluation of the detected tar species and classes offers another option to investigate the tar behavior over the PG cleaning path. In particular, the behavior of the tar conversion in the area of the hot gas filter, could provide information on future operating modes. Influencing variables such as temperature and filter cake thickness, measured via the pressure loss at the filter, could have an impact on the tar conversion and separation at this gas cleaning step. Another point for investigation is the separation rates for tars species as well as other impurities in the water quench and the RME scrubber.

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9 Abbreviation list

°C	Grad Celcius	H ₂	hydrogen
µm	mikrometer	H ₂ O	water
BTEX	benzene, toluene, ethylbenzene, xylene	H ₂ S	hydrogen sulfide
C	carbon	HCl	hydrogen chloride
C ₂ H ₄	ehylene	HCN	hydrogen cyanide
C ₂ H ₆	ethane	HF	hydrogen flouride
CaSO ₄	calcium sulfate	HNCO	isocyanide oxide
Cat.	category	ILS	internal loop seal
CCC	counter-current column	K ₂ CO ₃	potassium carbonate
CH ₃ SH	mercaptanes	kW	kilo watt
CH ₄	methane	l/min	liter per minute
CHP	combined heat and power	LHV	lower heating value
Cl	chlorine	LLS	lower loop seal
C _n H _m	tars	max.	maximum
CO	carbon monoxide	mbar	milli bar
CO ₂	carbon dioxide	MDEA	methyldiethanolamines
COS	carbonyl sulfide	MEA	monoethanolamines
CR	combustion reactor	mg	milli gram
CS ₂	carbon disulfide	MJ/Nm ³	mega joule per norm cubic meter
C _x H _y	hydrocarbons	mol/l	mol per liter
daf	dry and ash free	MP	measurement point
db	dry basis	MW	mega watt
DEA	diethanolamines	N	nitrogen
DFB	dual fluidized bed	n. I.	no information
e. g.	exempli gratia (for example)	N ₂	nitrogen
ECN	Energy research Centre of the Netherlands	N ₂ O	nitrous oxide
ESP	electrostatic precipitators	NH ₃	ammonia
et. al.	et alii	NO _x	nitrogen oxides
FG	flue gas	O ₂	oxigen
FT	Fischer-Tropsch	PAH	polycyclic aromatic hydrocarbon
g/mol	gram per mol	PG	product gas
g/Nm ³	gram per norm cubic meter	ppb	parts per billion
GC	gas chromatography	ppm	parts per million
GC/MS	gas chromatography coupled with mass spectrometry	PV	photo voltaic
GHG	greenhouse gas	RME	rapeseed methyl ester
GR	gasification reactor	S	sulfur
grav.	gravimetric	S ₂	sulfur
h	hour	syngas	synthesis gas

Abbreviation list

th	thermal
TU	technical university
ULS	upper loop seal
v	volumetric
vol.-%	volumetric percent
WC	wood chips
WC/R	wood chips Cat. 1 with rejects 1/1 wt.-% blend
wt.-%	weight percent

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