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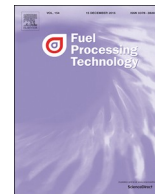
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Research article

Steam gasification of biomass – Typical gas quality and operational strategies derived from industrial-scale plants

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ABSTRACT

Steam gasification enables the thermochemical conversion of solid fuels into a medium calorific gas that can be utilized for the synthesis of advanced biofuels, chemicals or for heat and power production. Dual fluidized bed (DFB) gasification is at present the technology applied to realize gasification of biomass in steam environment at large scale. Few large-scale DFB gasifiers exist, and this work presents a compilation and analysis of the data and operational strategies from the six DFB gasifiers in Europe. It is shown that the technology is robust, as similar gas quality can be achieved despite the differences in reactor design and operation strategies. Reference concentrations of both gas components and tar components are provided, and correlations in the data are investigated. In all plants, adjusting the availability and accessibility to the active ash components (K and Ca) was the key to control the gas quality. The gas quality, and in particular the tar content of the gas, can conveniently be assessed by monitored the concentration of CH₄ in the produced gas. The data and experience acquired from these plants provide important knowledge for the future development of the steam gasification of biomass.

1. Introduction

Steam gasification of biomass enables the production of a gaseous secondary energy carrier with a calorific value typically in the range of 12–14 MJ/m³. The produced gas can be conditioned and thereafter utilized in a variety of processes, such as synthesis [1] and fermentation [2] to produce different products. Therefore steam gasification of biomass offers an attractive route for fossil-free production of advanced biofuels and materials and the generation of heat and power [3]. As of today, the large-scale examples of steam gasification of biomass are based on the dual fluidized bed (DFB) technology, which consists of two connected fluidized bed (FB) reactors. One reactor is used for gasification (Fig. 1) while the second reactor is used to produce the heat required for the gasification process through combustion of the char left after devolatilization and partial gasification. The heat generated is transported to the gasification chamber by circulating a bed material, which is made of particles with diameters in the range of 0.2–0.8 mm, and typically heating the gasifier to 800°–870 °C. In this DFB configuration, the char is not the final product, but it is the fuel to generate the heat required in the process. Other gasifier configurations may be

considered in future gasification plants, with alternative heating sources than the char combustion, e.g. off gas from synthesis processes or electric heating. Yet the chemical reactions occurring in the gasifier section of the DFB are of relevance to any type of steam gasifier solution, as well as the challenges associated to the downstream cleaning of the gas (right-hand side of Fig. 1).

A major challenge in gasification processes is the amount and number of contaminants in the produced gas that need to be removed before utilizing the gas. The contaminants in the gas determine the design and operation of downstream gas conditioning equipment, where it is crucial to limit fouling [4]. In particular, the gas cooling is a challenging step, during which the equipment can become clogged with ash, particles or tar, or a mixture of all three [5]. The present work is, therefore, focused on the gas quality and trends in the concentrations of the gas to facilitate the design and operation of steam gasifier as well as the development of downstream equipment. The experience from 6 state-of-the-art DFB gasifiers with at least 2 MW of thermal input is reviewed and analyzed. This analysis is based on the experimental experience as well as on more than 180 experimental data-points with gas and tar analysis acquired from in these units. The plants included in the

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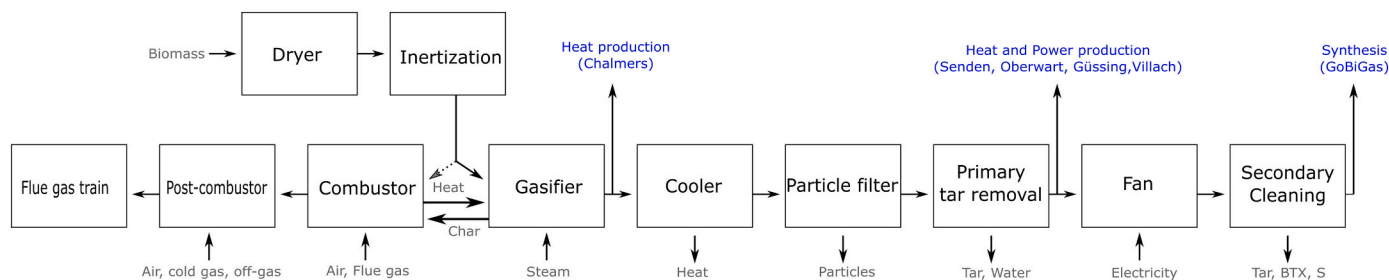


Fig. 1. Typical process steps included the gas production section of a DFB gasification-based plant. The required downstream equipment is different for different end-products and are indicated with blue text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Industrial-scale dual fluidized bed gasifiers included in this study.

Plant	Senden	Oberwart	Villach	Güssing	GoBiGas	Chalmers
Period of operation	2012–2018	2008–2014	2010–2012	2002–2016	2014–2018	2008–present
Owner	Blue Energy Syngas	Wopfinger/Baumit	Wopfinger/Baumit	GREG	Göteborg Energi AB	Göteborg Energi AB
End-product	Heat and power	Heat and power	Heat and power	Heat and power	Biomethane	Research (Heat)
Thermal input (MW, LHV)	14	8.5	15	8	30–35	2–4
Considered commercial scale (MW)	5–50	5–50	5–50	5–50	> 100	> 100

study are listed in Table 1. In the Senden, Oberwart, Güssing and Villach plants the gas is used for heat and power production and it needs to be cleaned of particles and tar, to avoid fouling. In contrast, the GoBiGas plant was designed for the synthesis of advanced biofuels and the gas needs to be more extensively cleaned to protect downstream catalysts from poisoning and cooking (see Fig. 1). In all these instances, the gas needs to be cooled to maximize the heat recovery within the plant.

The tar yield and composition from steam gasification is affected by a multitude of parameters, including the feedstock, temperature, steam ratio, mixing, heating rate, residence time, addition of catalytically active components, and also on the choice of bed material [6–9]. The roles of the different active components used in gasification processes have recently been reviewed by Arnold and Hill [10], who pointed out that alkali metals, such as potassium and sodium, alkaline-earth metals, such as calcium and magnesium, and heavy metals, such as iron and nickel, have all been applied to catalyze gasification reactions. Despite their catalytic activity, heavy metals have not been applied to any of the investigated large-scale DFB gasifiers due to their relatively high price, resulting contamination of the ash and/or oxygen transport capability. Large units have limited their choice of active species to the components already present in the biomass ash, mainly potassium (K) and calcium (Ca). Other ash elements present in the fuel ash and/or in the bed material should also be considered, as they can inhibit the active species, e.g. by forming inactive silicates or aluminosilicate compounds in the case of silicon and alumina.

A significant difference between potassium and calcium species is the high mobility of the volatile potassium compounds compared to the less-volatile calcium compounds [10–14]. The high mobility confers a strong activation towards char gasification upon some potassium species, as they can penetrate and intercalate with carbon in the char [10]. A strong impact of potassium addition on the tar yield has also been reported, which can be related to the homogeneous gas-phase reactions of the volatiles [15–18]. The volatile nature of the potassium compounds also leads to continuous loss of potassium with both the product gas and flue gas [19]. High concentrations of mobile potassium components can cause fouling in downstream equipment as the gas is cooled [5,19], which must be considered in both the design of the cooler and the operational strategy if additives containing K are used.

Calcium mainly remains as solid components forming active sites on the surface of the bed material. Due to its lower mobility compared to potassium species, calcium is less active towards char gasification and in homogeneous gas-phase reactions. The loss of calcium in fluidized

bed systems is rather due to attrition and fine particles leaving the process. The formed active sites catalyze cracking of mature tar components, and Ca can also be used as a secondary measure for downstream tar reduction [20–22]. Calcium can also work as an adsorbent of CO₂, which is generally an undesired part of the product gas, so it can to some extent be used to reduce the downstream need for CO₂ removal [23]. Such processes are frequently referred to as *sorption-enhanced reforming* (SER).

Synergetic effects from potassium and calcium addition have been reported in the literature [24], which can be attributed to the formation of eutectic phases that increase mobility of the active species. However, this can cause blocking of pores or even agglomeration [10]. Calcium can also prevent the deactivation of alkali components, such as potassium, by preferentially forming silicate or aluminosilicate species and leaving potassium as the catalytically active component [10]. This contributes to reduce the risk of agglomeration of bed material in DFB systems because calcium-silicates have a higher melting point than potassium silicate.

In all plants covered in this work, a catalytic reaction environment is created in situ during operation, with the steady supply of active components from the fuel ash to the process and the activation of the bed material. This makes it complicated to replicate and investigate the dynamics of such catalytic environment at the laboratory scale. Different strategies to enhance the catalytic activity have been applied at large scale such as recirculation of ash streams and/or the use of Ca and K-additives. Data from such large-scale operation are, thus, crucial for the future development of the technology and design choices. For commercial-scale DFB gasification applications, it is also important to understand the mixing in the fluidized beds, as this has implications on the heat transfer and chemical reactions [25]. Here, features related to the mobility of the active components, fuel feeding, and fluid-dynamics, as well as the exit of solids from the fluidized bed play important roles. By including DFB gasifiers with significant differences related to these features in the present work, the impacts of some important design choices can be discussed. Furthermore, it is complicated to perform controlled investigations and quantify all the parameters in a commercially operated plant. Previous work have reported evaluations of a few operational cases at large scale, e.g. [26,27] and comprehensive evaluations at smaller scale, e.g. [28], while a combined evaluation of commercial plants is currently lacking. The aims of this work is to facilitate the development of the steam gasification technology, as well as the downstream equipment by providing reference data and discussing

differences and similarities in design and operational strategies used at commercial DFB gasifiers.

2. Methods

2.1. Plant description

The DFB gasifiers in focus here differ in terms of the end-product, thermal input, feedstock, operational strategies, and the scale considered appropriate for a commercial plant. Two of the industrial-scale plants – GoBiGas and Senden – will be described in more detail as most of the data-points presented here come from these plants. The research gasifier at Chalmers with 2–4 MW_{th} input has been included, as it has enabled investigations over a wider range of operation than commercial plants with complete downstream equipment and it also provided data points with unique operation features, e.g., silica sand as bed material. The plants in Güssing [29], Oberwart [30] and Villach [36] have been described in previous publications, and only single points are included in the following diagrams.

2.1.1. The GoBiGas plant

The GoBiGas plant was built by Göteborg Energi AB to demonstrate that biomethane could be produced from woody biomass. The gasifier was built by Valmet OY under license and designed by Repotec to have a thermal input of about 32 MW (LHV dry ash-free fuel) and to produce 20 MW of biomethane. The goal of the project was to demonstrate the feasibility of the technology for the construction of a commercial plant with production level of about 100 MW of biomethane [5]. An overview of the process is shown in Fig. 2.

The GoBiGas plant was mainly operated with wood pellets, although wood chips, shredded bark, and recovered wood (class A1) were also tested as feedstocks. The project and commissioning of the plant have been previously described in detail [5]. In summary, the major challenges for operation of the plant were related to the gas cooling and fuel feed, and these issues were resolved by adapting the operational strategy. Calcium, which was added indirectly to the process as calcium carbonate, was used as a pre-coat (continuously fed) for the product gas particle filter. The particles from the filter were recirculated to the

combustion reactor for energy recovery from the char, soot and tar captured by the filter, as well as to feed the calcium to the process to activate the bed material. However, sufficient reduction of the tar yield could not be achieved through activation by the pre-coat, and the fuel ash before the tar caused clogging of the cooler. The tar yield was, therefore, further reduced by feeding potassium carbonate dissolved in water (40%) to the combustion side of the process, which was transported to the gasification reactor by the bed material where it was released as active components. This reduced the concentrations of the tar components to such an extent as to enable continuous operation without clogging the cooler. Furthermore, the temperature of the process was reduced to decrease the loss of potassium with the flue gas, thereby simplifying the buffering of potassium during start-up, as re-activation is required after the process is heated for start-up using an ash free fuel in the form of natural gas [31].

The main challenge related to the fuel feed was that the conveyor screw that fed the fuel to the gasifier was clogged as fuel was pyrolyzed already in the screw. This was mitigated, though not completely resolved, by reducing the bed material inventory of the process to feed the fuel close to the surface. It turned out that the coarse ash from the flue gas, which was co-fed with the fuel to recover important ash components to the process, was accelerating the clogging of the screw. After discontinuing the co-feeding of ash and operation with a lower bed, process stops due to clogging of the fuel-feeding screw was avoided [5].

The bed material used was olivine. Initially, Austrian olivine that was pre-calcinated was used but this was later exchanged for Norwegian olivine without pre-calcination. Thus, the greenhouse gas emissions related to the bed material were significantly reduced by reducing the olivine transport distance and avoiding the pretreatment step. There was no significant change in the process due to the change of bed material and addition of both K and Ca was required with both materials to achieve sufficient activation for the GoBiGas plant.

Other relevant features of the GoBiGas gasifier were that the fluidized bed partially consisted of an inclined wall section that was not fluidized. The fuel was fed close to the surface of the bed in the inclined section. Bed material and char particles were circulated back to the combustion via a chute that was located below the surface of the bed in

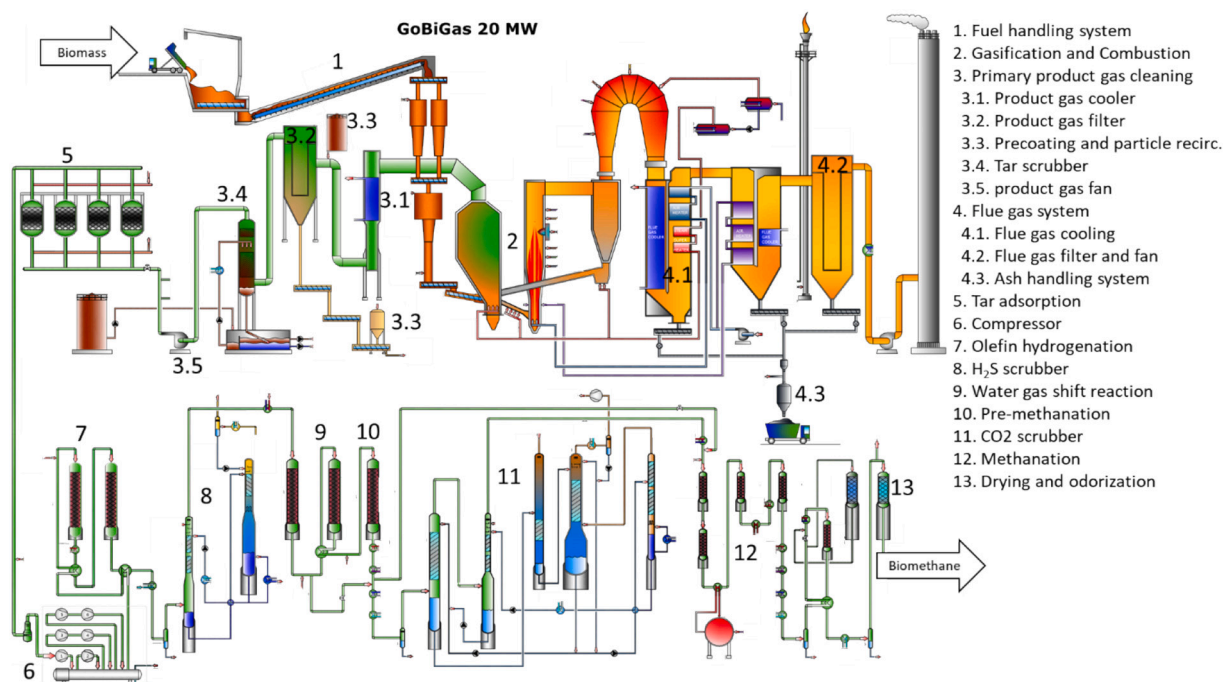


Fig. 2. Schematic of the GoBiGas plant, from [5].

the gasifier so that the char had to be submersed in the bed in order to leave the gasifier. The bottom ash and part of the bed material were continuously extracted from the bottom of the gasifier when operating with fuels other than wood pellets, to prevent the accumulation of undesired ash components, such as silica, in the system.

2.1.2. The Senden plant

The Senden DFB power plant was designed to have a fuel power of 15 MW_{th}, generating about 5.1 MW_{el} in two gas-fired engines and using an organic Rankine cycle (ORC), and it also produced about 6.4 MW_{th} of district heat. The gasifier was built by Ago AG and was designed by Repotec.

In the Senden plant, logging residues from forestry are used as the feedstock. This feedstock is more heterogeneous than pure stem wood, as it includes bark, cut-off root ends, tops, branches, needles, and leaves. In previous studies, it was stated that this feedstock contains on average 15% bark and 15% needles and leaves [32]. Moreover, it varies widely in terms of its particle size distribution and moisture content. In a previous work [33], it was shown that significant amounts of foreign mineral matter, mostly quartz, are carried into the gasification reactor together with the biomass. The mineral matter most likely originates from the harvesting and handling procedure. However, the authors do not have detailed information on the origin of the foreign matter. Larger foreign matter grains are periodically discharged from the reactor when releasing a certain amount of ash from the bottom of the combustion reactor. This bottom ash comprises the regular olivine bed material, foreign matter grains, and bottom ash. It has been shown in a previous study that this foreign mineral matter has a negative influence on the operation of the DFB gasifier of the power plant [32].

The biomass is collected onsite in four storage silos before being fed into the biomass dryer. Through constant mixing of the feedstock, achieved by periodic collection from different storage silos, the biomass is homogenized before being brought into the gasification reactor. Homogenization is ensured by a feedstock management plan that is executed onsite by the staff of the power plant.

Compared to the GoBiGas plant, the operational strategies chosen to improve the performance of the Senden power plant were different. The tar yield was reduced by achieving activation of the bed particles through ash layer formation that led to calcium-rich surfaces. Calcite was used as an additive during the start-up phase of the process, to achieve faster activation of the particles. To enhance this strategy, re-use of the already ash-layered bed and sieved material was enabled by recycling recovered material that was discharged from the reactor together with impurities. For this purpose, an additional bed material silo for used olivine was installed (Fig. 3, 1a and b). The recovered olivine was added instead of fresh olivine, to compensate for bed material losses. Furthermore, coarse ash from the flue gas train was recovered and recycled to the combustion section of the process, to reduce the loss of activated bed material. Periodically, the coarse ash was discharged from the system to avoid the accumulation of low-melting-point components, which resulted from reactions of alkali with silica-rich ash or quartz particles that entered the reactor together with the fuel (Fig. 3, 1c). In addition, the mixing of biomass and bed material was improved by introducing additional fluidization nozzles into the inclined wall (or slope) of the gasifier (Fig. 3, 2).

Coarse ash particles were initially recirculated into the feeding screw. However, early on in the operation, the recirculation was changed so that it fed directly into the combustion reactor, so as to decrease the mechanical stress in the feeding screw. The feedstock was transported into the fluidized bed and the pyrolysis of biomass inside the screw was kept to a minimum by cooling the screw. Nevertheless, it is important to point out that the feeding screw played a critical role throughout the operation and operation times > 2000 h without problems with the screw could be realized.

2.1.3. The Chalmers gasifier

The Chalmers gasifier was constructed and designed by Metso (now Valmet) in collaboration with Chalmers University of Technology and Göteborg Energi AB as a retrofit of an existing CFB boiler to create a DFB system (Fig. 4). The purpose of the plant was to facilitate research at an industrial scale with input of 2–4 MW_{th} and with the gas being combusted in the CFB boiler, providing district heating. The plant has been described in detail previously [34]. In summary, the bed material from the CFB is directed to the gasifier via a loop seal that is fluidized with steam and the fuel is fed at the top of the bed, in contrast to the Senden and GoBiGas gasifiers. The bed material and unconverted fuel exit the gasifier from the top of the bed, passing a weir before entering another loop seal that transports the material back to the CFB. Additional biomass is fed to the CFB, which means that the gasifier can be operated over a wide range of operational parameters, as specific operation of the gasifier is not required for stable combustion operation. With the additional biomass fed to the combustor, additional amounts of active ash components are continuously added to the process, activating the bed material even when fuel or additives are not fed into the gasifier. Furthermore, an elaborate system has been developed to enable quantification of all the mass and energy flows from the process [35].

2.2. Operational strategies

Table 2 gives an overview of the additives chosen, together with the bed material used in each plant. The operational strategies of the power plants in Senden, Oberwart, Villach and Güssing are different from those applied at the Swedish GoBiGas and Chalmers plants. While the former relies on the effects of the addition of calcium and fuel ash, the latter relies on the addition of potassium together with calcium addition and the fuel ash. Thanks to the synergetic effects between Ca and K, the two activation strategies are complementary to each other and are not mutually exclusive. The extent of which active component should be dominantly encouraged is dependent of the ash composition of the feedstock and the implications that arise from it, e.g. agglomeration issues. To illustrate how deactivation of the active components affects the gas composition and tar concentrations, cases operated with silica sand are included in present work, extending the investigated dataset to include very low activation levels.

Typical values for the investigated process parameters, as well as the design features and feedstocks are presented in Table 3. Three commonly monitored operating parameters that reflect the severity in the gasification process are: bed temperature of the gasifier bed; volume flow of the dry gas, which indicates the gas hourly space velocity (GHSV) of the gasifier; and steam used for the fluidization of the gasifier, indicating the fluidization velocity, as well as the steam-to-dry gas ratio. The dry gas hourly space velocity out is based on the gross flow of dry product gas (normal condition) out from the gasifier, which is commonly used to indicate the load of the gasifier and regulate the fuel feed. It also gives a qualitative indication of the residence time of the produced gas in the gasifier. The actual flow and moisture contents of the fuel are not measured at the commercial plants. Therefore, instead of the commonly used steam-to-fuel (STF) ratio, the steam-to-dry gas ratio is introduced here and is based on the flow of dry gas and the steam used for fluidization of the gasifier. The addition of steam is important for the mixing, as well as for the reactions in the reactor. Therefore, the loads of steam per unit of dry product gas in the bed section and in the freeboard section of the gasifier are compared here. The pressure-drop over the FB in the gasifier reflects the mass of the bed material inventory of the gasifier.

The bed material used in the large scale DFB gasifiers is olivine, which is a magnesium iron silicate that has limited catalytic properties by itself but that can be activated by the fuel ash or additives containing calcium and potassium [20,37–39]. Olivine has a low content of silicate

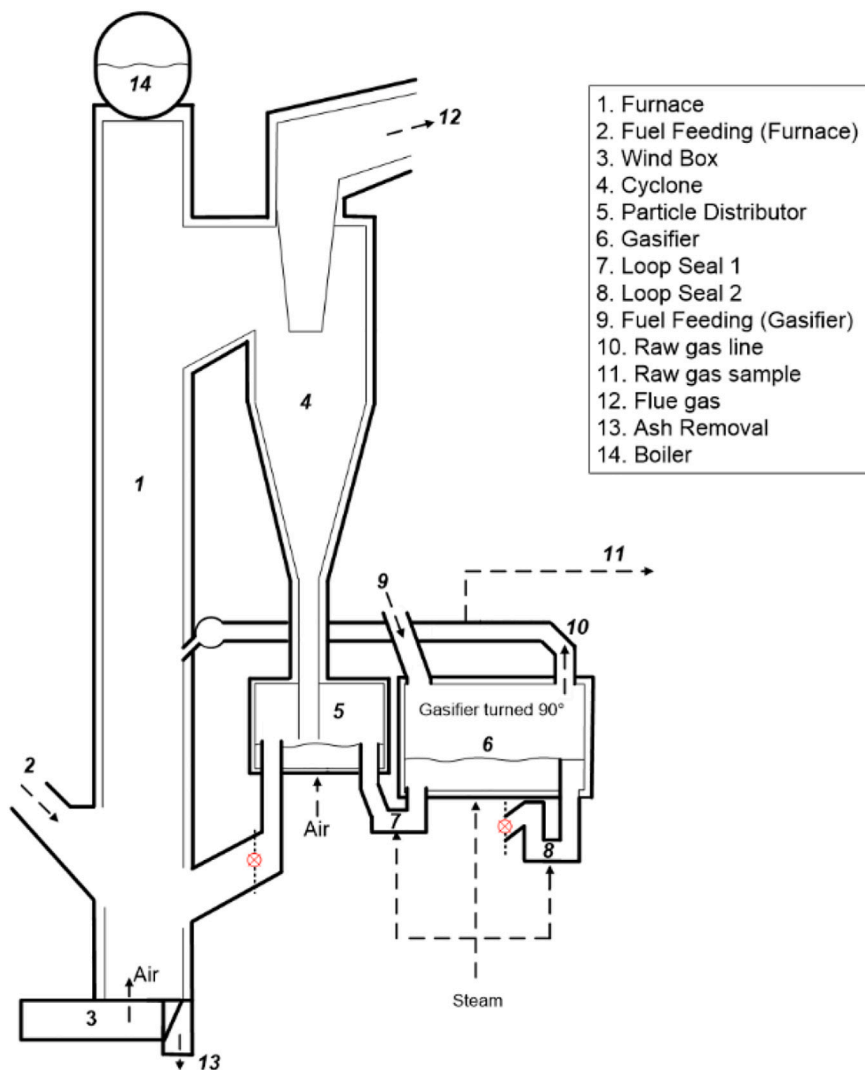


Fig. 4. Schematic of the Chalmers gasifier.

have been identified as enabling a qualitative analysis of the correlations between the operational parameters and the gas and tar concentrations.

The tar components included in the analysis are summarized in Table 6, with a representative component from each of the tar groups previously established in the literature [22]. Another frequently used system for tar component categorization is to divide the components into primary, secondary, and tertiary tar components [44]. Primary tar components, which are formed during the initial conversion process, react to form the secondary and, subsequently, the tertiary tar components as the severity of the process increases, commonly referred to

as the ‘maturation’ of tar. The term ‘severity’ is here used to describe the combined effect of parameters that affect the reaction rate, such as temperature, residence time, and concentrations of reactants. Primary tar components may be present in low concentrations at low severity, and can be quantified indirectly [35]. To avoid high-level uncertainties due to significant amounts of primary tar components, the dataset is limited to including only those cases with a bed temperature $> 745\text{ }^{\circ}\text{C}$.

Large polyaromatic hydrocarbons (PAHs) of tar group 5 have a high dew-point and, therefore, there is a risk that they will foul on cold surfaces, such as those in the cooler. Pyrene consists of four aromatic rings ($\text{C}_{16}\text{H}_{10}$) and is here chosen as representative of group 5

Table 2

Overview of the operational strategies applied at the investigated plants.

Activation strategy	Senden	Oberwart	Villach	Güssing	GoBiGas	Chalmers
- Silica, no additives						X ^a
- Olivine, no additives						X
- Olivine, Ca addition	X	X	X	X	(X) ^b	X
- Olivine, K addition					X ^c	X

^a Included for reference cases with low levels of activation.

^b Initially tested with clogging of the downstream cooler as the result. All data-points acquired from the GoBiGas plant with a CH_4 concentration $> 9\%$ are without the addition of K.

^c Calcium was also added at GoBiGas for all the cases, as CaCO_3 was used as pre-coat of the product gas particle filter and then continuously fed to the combustion part of the process.

Table 3
Typical values for the investigated design and operational parameters.

	Senden	Oberwart	Villach	Güssing	GöbIGas	Chalmers
Fuel	Logging residues	Wood chips	Wood chips	Wood chips	Wood pellets, Wood chips, Shredded bark, Recovered wood (A1)	Wood pellets, Bark pellets
Fuel moisture	~22% after the dryer (> 33% when delivered)	~18% after the dryer (> 33% when delivered)	> 33%	23%–35% (no dryer)	7%–35% (no dryer)	7%–10%, Pelletized fuel ^a
Temperature of the gasifier bed (°C)	820–860	860–880	~860	~870	790–870	760–850
Temperature of cooling media (°C)	135	~135	~135	~135	160	–
Dry GHSV out ($m^3_{dry,out} h^{-1} m_{reactor}^{-3}$)	102–154	100–120	~102	~105	19–105	62–149
Steam-to-Dry Gas ratio ($kg_s m_{dry,out}^{-3} m_{bed}^{-2}$)	0.29–0.65	0.32–0.37	0.33–0.35	0.33	0.42–1.90	0.33–1.22
Fluidization ($kg_s h^{-1} m_{bed}^{-2}$)	500–1500, conical bed	500–1500, conical bed	600–1600, conical bed	600–1500, conical bed	1150–1700, conical bed	110–180
Dp_{bed} (mbar)	230–267	~166	~170	~106	180–260	110–180
Fuel feed	80–160	70–90	70–100	80–90	70–90	~60
Solids exit	In bed screw	In bed screw	In bed screw	In bed screw	Bed surface screw	Surface, Down-comer
Outline of the fluidized bed section of the gasifier	Partially inclined, completely fluidized ^b	In bed	In bed	In bed	In bed	Top, weir
	Partially inclined, no fluidization in inclined section	Partially inclined, no fluidization in inclined section	Partially inclined, no fluidization in inclined section	Partially inclined, no fluidization in inclined section	Partially inclined, no fluidization in inclined section ^c	fluidized uniformly, no inclined section
Reference	[32]	[30]	[36]	[29]	[5]	[34]

^a Can also be operated with chipped fuel that has a higher moisture content (not included in present study).

^b Fluidization of the inclined part of the bed was added in Year 2016.

^c Bed height was reduced, which limited the inclined and defluidized areas.

Table 4
Summary of features related to the active components potassium and calcium.

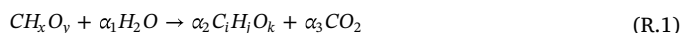
Species	Features
Potassium (K)	<ul style="list-style-type: none"> • High mobility • Able to intercalate with carbon • Change reaction path for volatiles • Low activity towards mature tar • Can cause agglomerations • Can be transported by the bed material, which acts as a carrier
Calcium (Ca)	<ul style="list-style-type: none"> • Non-volatile • Promotes tar cracking • CO₂ sorbent • Reduce risk of agglomeration at relevant temperatures • Forms catalytically active sites on the bed particle surfaces

components, being one of the most abundant members of this group. Pyrene, as well as naphthalene and benzene are tertiary components that are formed by the reformation and polymerization of secondary tar components and saturation of alkyl tertiary species. Naphthalene and components with more aromatic rings (of groups 3–5, with some from group 6) are mainly removed from the product gas in the primary tar cleaning step, whereas benzene (group 1) and other light homogeneous components (group 2) and some heterogeneous components (some of group 6) require a second product gas cleaning step. When the SPA method was used without included active carbon in addition to the amine the measured concentrations of benzene, phenol and styrene was excluded.

Measurements of pyrene and 2-methylnaphthalene are included only for the samples taken prior to the particle filter, as a significant proportion of these components can be removed from the gas by the filter. A sampling-filter heated to above 300 °C was used for some measurements, but has previously been shown not to affect the tar measurements [42] and the measured pyrene concentrations from these measurements are assumed to be representative and therefore included in the analysis. Naphthalene, benzene, phenol, benzofuran, and styrene have lower tar dew-points and are assumed to be accurately sampled after the particle filter. It should be noted that since there are no measurements available for the concentration of steam, the tar

concentrations are presented as concentrations in the dry gas under normal conditions.

The main gas components in the gas are H₂, CO, CO₂, CH₄ and C₂H₄ and they are included in the analysis to investigate how they correlate with the investigated process parameters and concentrations of selected tar components. The syngas components H₂, CO and CO₂, and more specifically their H/C-ratio and O/C-ratio are of interest to estimate the potential performance of a downstream synthesis process, to do a qualitative analysis of the fuel conversion in the gasifier [45] and they also help detecting poor activation or outliers linked to deviations in the process, sampling or measurements. When it comes to assessing the fuel conversion, the H/C and O/C ratios of the syngas are very sensitive to the extent of the water-gas shift (WGS) reaction (CO + H₂O → H₂ + CO₂), which also affects the yield of dry gas and, thereby, the concentrations of the measured tar components. By plotting the H/C-ratio as a function of the O/C-ratio, it can be illustrated if the differences in data-points are due exclusively to a difference in the WGS reaction or not. Thus, these ratios could even be implemented to monitor the fuel conversion in a gasifier online [31]. In relation to the potential performance of a downstream synthesis process, the H/C and O/C ratios are convenient to estimate the theoretical carbon utilization and efficiency of a downstream synthesis process based on the global reaction:



The theoretical degree of carbon utilization, meaning the amount of carbon that can be reallocated into the final product based on stoichiometry of R1, is given by Eq. (1) (previously derived in [45]):

$$\mu_{C,theoretical} = \frac{\left(1 - \frac{1}{2} \left(\frac{O}{C}\right)_{syngas} + \frac{1}{4} \left(\frac{H}{C}\right)_{syngas}\right)}{\left(1 - \frac{1}{2} \left(\frac{O}{C}\right)_{prod.} + \frac{1}{4} \left(\frac{H}{C}\right)_{prod.}\right)} \quad (1)$$

For instance, if the end-product is Fisher Tropsch (FT) crude with a H/C-ratio of 2.1, then 40%–48% of the carbon in the product gas can theoretically be synthesized into FT crude for the cases with moderate or strong activation. This can be compared with the theoretical maximum based on the complete conversion of wood pellets (H/C = 1.43

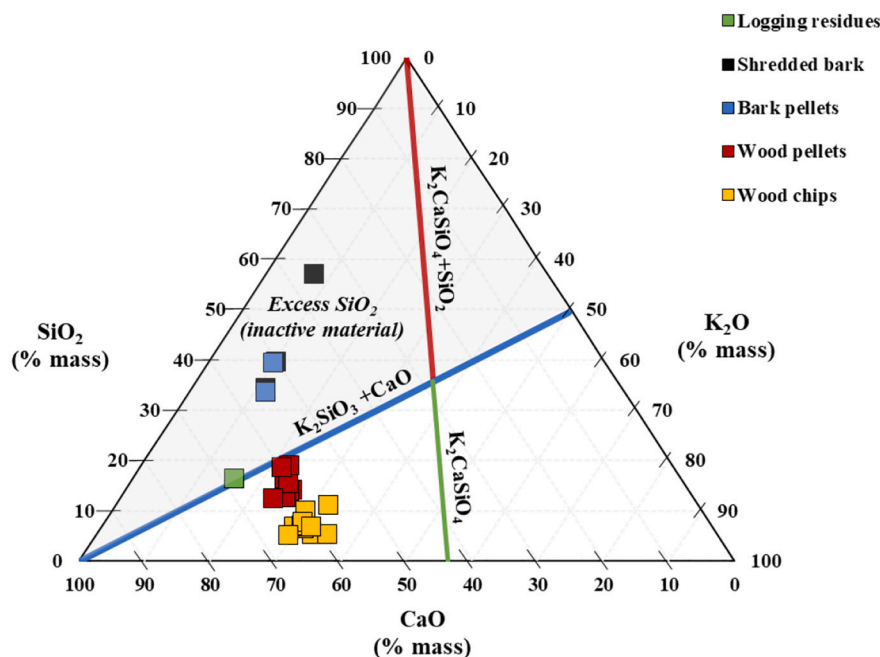


Fig. 5. Si, K, and Ca compositions of the fuel ashes for different fuels. Solid lines correspond to the stoichiometry of the indicated silicate. The shadowed area refers to the ash composition with an excess of SiO₂ with respect to the stoichiometric amount required to form silicates.

Table 5
Previous univariate studies of the effects of the different process parameters.

Parameter	Gasifier	Units	Range	Comments	Ref.
Bed temperature, ash	Chalmers	°C	768–848	Fresh olivine	[6]
Bed temperature, Ca	Senden	°C	832–853	Ca addition	[7]
Bed temperature, K	Chalmers	°C	746–829	K addition	[6]
Activation	Chalmers	–	–	Fresh to activated with fuel ash and fresh to K addition	[6]
Residence time	Chalmers	s	4.0–5.5	Change of fuel and steam for constant STF	[8]
STF ratio, silica	Chalmers	kg/kg _{daf}	0.86–0.98	Change of fluidization	[8]
STF ratio, olivine	Chalmers	kg/kg _{daf}	0.85–1.22	Change of fluidization	[9]
Bed inventory	Senden	mbar	89–155	Pressure drop over the fluidized bed of the gasifier	[7]

and O/C = 0.65), for which 68% of the carbon in the fuel could be utilized for the production of FT crude. However, this would require the addition of heat from an external source.

Furthermore, the O/C-ratio can be used to determine whether the difference in the concentration of tar at two separate measurement points is the result of dilution of the dry product gas due to the WGS reaction. As the WGS reaction is equimolar, it does not affect the concentrations of tar components in the wet product gas. However, as tar concentrations are measured on a dry gas basis, the WGS reaction will affect the measured concentrations. Based on the stoichiometry of the WGS reaction, the potential change in tar concentration ($C_{tar, comp}$) depends on the concentrations of CO and CO₂ (C_{CO+CO_2}) and can be estimated as function of the O/C-ratio based on CO and CO₂ as follows:

$$C_{2, tar, comp.} = \frac{C_{1, tar, comp.}}{\left(1 + C_{CO+CO_2} * \Delta\left(\frac{O}{C}\right)_{1 \rightarrow 2}\right)} \quad (2)$$

3. Results and discussion

3.1. Overview of gas composition

The typical concentrations of the main gas components in the dry product gas for all the investigated cases are summarized in Fig. 6 as a function of temperature. Each gasifier is represented by a symbol and the different colors indicate different bed material or fuel.

The data shows significant scatter, which cannot be explained by differences in the bed temperatures of the gasifiers. The data obtained from operation of the Chalmers gasifier with silica sand as the bed material is clearly segregated from the rest. This segregation is attributed to the low catalytic activity of silica sand as compared to that of olivine. Limited contributions to this segregation are expected from other scale and shape factors, as the data derived from the Chalmers gasifier using active olivine is similar to that obtained in the larger

units. In contrast, the data-points from operation with olivine for the six gasifiers and with different biomass fuels are less scattered. A more detailed analysis is required to understand the dynamics (e.g., status of activation) of these gasifiers.

3.2. H/C-ratio versus O/C-ratio

Fig. 7 shows the H/C-ratio and O/C-ratio of the syngas components (CO, CO₂ and H₂), as well as dotted WGS reference lines. For two points that differ in ways other than just the WGS direction, it can be concluded that other reactions, such as the conversion of hydrocarbons or char into product gas, must have occurred to different extents. The reforming of hydrocarbons and gasification of char into product gas will shift the coordinates to a WGS line with a higher H/C-ratio, thereby indicating increased conversion of the fuel into product gas components. However, it should be noted that when there is addition of CO₂ as a purge gas or of O₂ to the gasifier the coordinates are moved to a WGS line with a lower H/C-ratio, counteracting the increased conversion of the fuel.

The figure shows significant segregation of cases with weak catalytic activation from cases with moderate or strong activation. With weak activation, the WGS reaction is less prominent and the cases are located along WGS lines with a lower H/C-ratio, indicating a lower conversion of hydrocarbons and char into product gas. For cases with moderate or strong activation, all data-points from different gasifiers or different fuels lay in a rather narrow region.

Based on the cases with weak activation in Fig. 7, 34%–41% of the product gas (syngas) can be potentially utilized in a downstream synthesis process, recall Eq. (1). There is an overlap in the potentials for carbon utilization, although most of the cases with moderate or strong activation offer a higher level of carbon utilization than those cases with weak activation. Note that the hydrocarbons in the product gas would need to be reformed into syngas to be utilized, and they are not

Table 6
Representative tar components included in the analysis.

Component	Formula	Structure	Tar group ^a (description)	Maturity level ^b	Comment
Pyrene	C ₁₆ H ₁₀		5 (≥ 3 aromatic rings)	Saturated tertiary species	Risk to cause fouling in product gas cooler and particle filter grows with higher severity [44].
Naphthalene	C ₁₀ H ₈		3 (2 aromatic rings)	Saturated tertiary species	Main component for primary tar removal, increases with higher severity [44].
Benzene	C ₆ H ₆		1 (1 aromatic ring)	Saturated tertiary species	Main component for secondary tar removal, increases with higher severity [44].
Phenol, Benzofuran	C ₆ H ₆ O, C ₈ H ₆ O		6 (heterogenic aromatic compounds)	Secondary species	May react to become tertiary tar with increased severity [44]. Phenols have high solubility in water.
Styrene, 2-Methylnaphthalene	C ₈ H ₈ , C ₁₁ H ₁₀		2, 4 (branched aromatic compounds)	Alkyl tertiary species	May react to become saturated tertiary tar with increased severity [44].

^a Based on the tar groups [22].

^b As described by Milne and Evans [44].

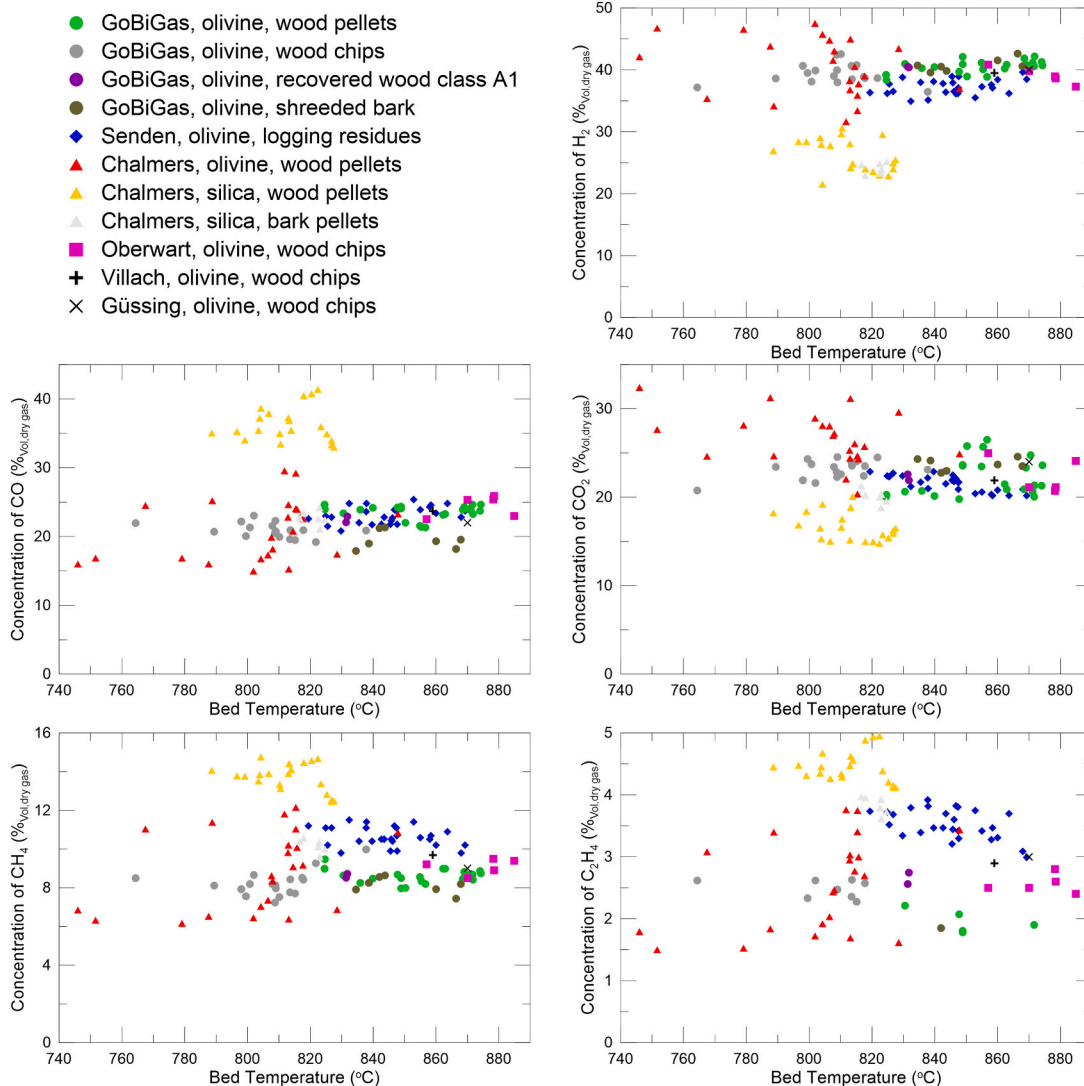


Fig. 6. Volumetric concentrations of the gas components of the dry product gas as a function of the temperature in the gasifier, with data shown for the GoBiGas, Senden, Villach, Güssing, Oberwart and Chalmers plants operating with the indicated bed material and feedstocks.

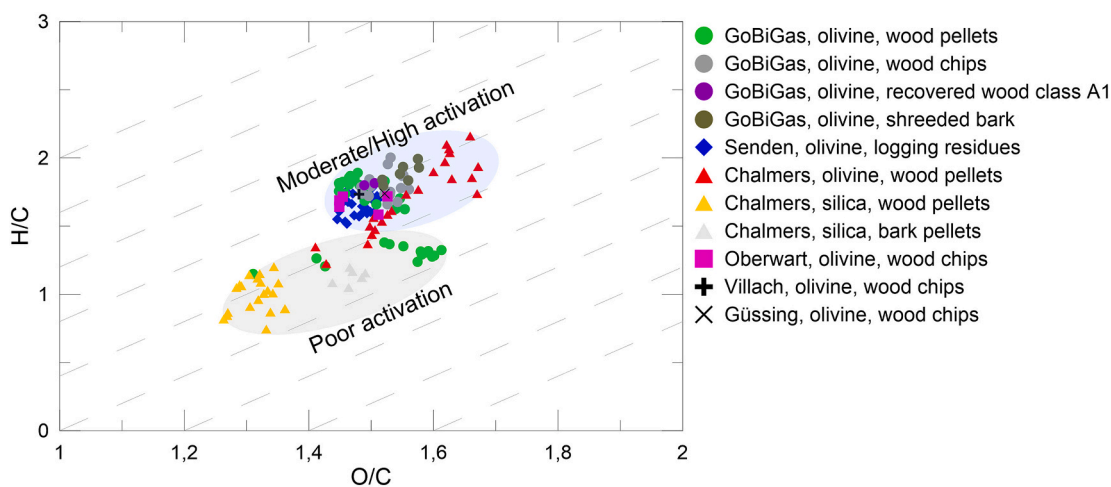


Fig. 7. Molar ratio of H to C (H/C) as a function of the ratio of O to C (O/C) of the product gas components H_2 , CO , CO_2 . The dotted lines are reference lines that indicate how the water-gas shift reaction would affect the coordinates. The scale of activation (weak-moderate-strong) is an arbitrary scale based on operational experience.

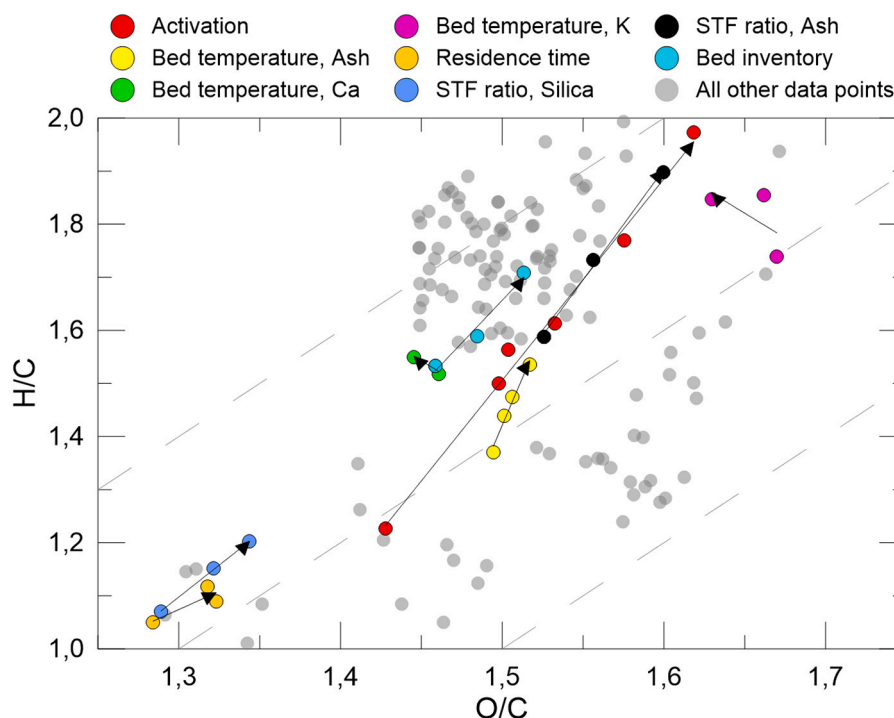


Fig. 8. Molar ratio of H to C (H/C) as a function of the ratio of O to C (O/C) of the product gas components H_2 , CO, CO_2 . The dotted lines are reference lines that indicate the direction of the water-gas shift reaction, and the colored points and arrows highlight different univariate studies.

included in the above example. Moreover, Eq. (1) does not include the energy balance and an external heat source may be required.

Fig. 8 emphasizes the data from the univariate studies included in Fig. 7. Each study is highlighted with a specific color, and the impacts of increasing the investigated operational variables are indicated by arrows. Increasing the level of activation (red dots in Fig. 8) and increasing the bed material inventory (cyan dots) yield similar slopes, indicating an increased WGS reaction and increased fuel conversion. With an activated bed material, *STF-ratio, Ash* (black) has a similar impact. However, with weak activation of the bed material, *STF-ratio, Silica* (blue) runs almost parallel to the reference WGS lines, indicating that there is little effect on the fuel conversion. The effect of temperature was investigated with different activation methods: fuel ash only (yellow), fuel ash and Ca (green), and fuel ash and K (purple). In all these cases, an increase in fuel conversion was observed. An increased residence time (orange) indicates no or even decreased fuel conversion. Note that both the residence time and *STF-ratio* were altered by changing the fluidization of the reactor, and they cannot be decoupled from the mixing effects.

As exemplified here, Figs. 7 and 8 can be used as a reference for a qualitative analysis of a DFB gasifier based only on the concentrations of H_2 , CO and CO_2 in the product gas. As more detailed measurements of the tar concentrations, as well as of the mass flow may be complex and time-consuming, this approach offers a cost-efficient method for tuning a DFB gasifier.

3.3. PCA analysis - variance in the dataset

By analyzing the variance in the dataset using a PCA, the strongest correlations between compounds and operational parameters were identified. The major part of the variation of the data (92% of the variance) can be described with only two PCs, where the first principal component (PC) of the PCA described 69% of the variance in the data, and the second PC described 23%. The contribution of a specific variable is called the 'loading', and the loadings of the different parameters for the first two PCs are shown in Fig. 9. Variables with a similar

loading are located in the same quadrant of Fig. 9 and can be expected to correlate positively, for example: the concentrations of naphthalene and C_2H_4 . Variables in opposite quadrants, for example: the bed temperature and concentration of phenol, indicate an inverse correlation, meaning that a lower concentration of phenol are to be expected at higher bed temperatures.

From the PCA results in Fig. 9, correlation to indirectly assess the activity of the bed towards tar can be derived. The concentrations of CH_4 and C_2H_4 and the H/C-ratio have previously been used as indicators of the level of activation of the bed material [5,17,31,46,47]. In Fig. 9, the concentration of CH_4 is located with a high value close to PC1, indicating that the catalytic activity of the bed correlates well with PC1. In simple terms, PC1 can be viewed as a coordinate that represents well the activation level of the bed material. The analysis also shows that either the concentration of CO or the H/C-ratio of the product gas components can be used to indicate the variance described by PC1, whereby the latter has been previously proposed as a good indicator of the level of activation of the bed material [17]. Furthermore, all the investigated tar components have a positive loading on PC1, indicating that the concentration of tar is generally higher with higher CH_4 concentration, suggesting a lower level of activation of the bed material.

The concentrations of several of the tar components, together with several measurable process parameters, including the bed temperature, fluidization in terms of steam flow related to the reactor area, and the volumetric loading of the reactor in terms of volume flow of produced dry gas in relation to reactor volume, show significant values along PC2. All of these parameters can be coupled to the thermal severity of the process.

The strong segregation of catalytic activation (PC1) from severity-linked parameters (PC2) in the PCA implies that the activation affects the gasification process differently from the thermal severity. These findings are in line with previous investigations that have proposed that the activation of olivine changes the reaction paths rather than promoting the reactions that predominates in the absence of catalytic species [17]. Based on the hypothesis that activation and severity have significantly different impacts on the product gas composition, the

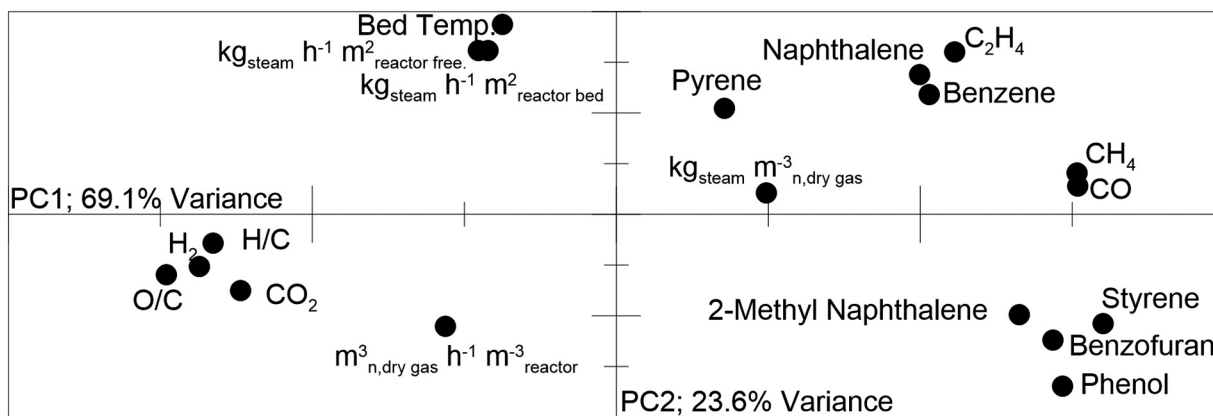


Fig. 9. Loading plot based on a principal component analysis (PCA) with pretreatment of the data involving unit variance (UV) scaling and mean centering. The first two PCs describes 69.1% and 23.6% of the variance in the data, respectively, and the lengths of the x-axis and y-axis are proportional to the % of variance described. The design parameters are defined in Table 3, and the tar components are listed in Table 6.

effects of bed material activation and severity are investigated separately. Note that a detailed analysis of the reaction mechanism and yields related to the dry fuel is outside the scope of this work. Instead, trends for the concentrations of specific tar components that are of importance for the downstream equipment are identified.

3.4. Activation level within the process

As indicated by the PCA, the H/C-ratio correlates well with the concentrations of the major tar components benzene and naphthalene (for naphthalene, Fig. 10, left), in agreement with previous investigations in the Chalmers gasifier [17]. However, this correlation is less relevant to commercial plants for biofuel production where CO₂ is likely to be used as purge gas, e.g. GoBiGas plant [5]. This will affect the H/C-ratio and make it sensitive to changes in the purge gas flow. Alternatively, a correlation between the concentrations of tar and C₂H₄ has also been suggested previously [17,47] and it is here confirmed for naphthalene (Fig. 10, right). However, online measurements of C₂H₄ are not applied as standard at the investigated industrial plants, but are instead assessed with complementing GC measurements.

The PCA also indicates that the O/C-ratio correlates with the tar concentration and an example for naphthalene is shown in Fig. 11. The potential dilution due to the WGS reaction is estimated according to Eq. (2) and shown in the figure for the case with the highest CO concentration of all the included data-points.

If this gas would have been shifted so as to have an O/C-ratio of 1.7 the amount of dry gas would increase and dilute the tar concentration by about 20%. As the extent of dilution depends on the concentrations of the dry product gas components at each data-point, a general trend cannot be readily identified for all the data-points. However, it can be concluded that for all the cases a shift towards an O/C-ratio of 1.7 yields a dilution of 1%–20%. Thus, it is confirmed that the WGS reaction does not explain the large differences in the measured concentrations of naphthalene.

An alternative is to use the correlation between the tar concentrations and concentrations of CH₄, which are easily measured online in commercial plants. This correlation has also been shown to be useful for automatically regulating the amount of K₂CO₃ added to the GoBiGas gasifier to adjust the activation level [5]. The concentration of CH₄ was also used as an indicator of an active bed material in the Senden plant. At Senden, threshold values were defined for the CH₄ concentration, and when the threshold values were surpassed the amount of the additive calcite was adjusted until the CH₄ concentration lay within the desired range. Besides varying the level of additive, the recovered bed material could be used in place of fresh olivine as make-up for bed material loss so as to increase the bed activation level. This material can be conveniently fed to the combustion reactor using the same feeding system as for the fresh material. The recycled bed material should not be recycled with the fuel feed to the gasifier if in-bed screw feeding is being used, as this will worsen the fouling-related problems in the

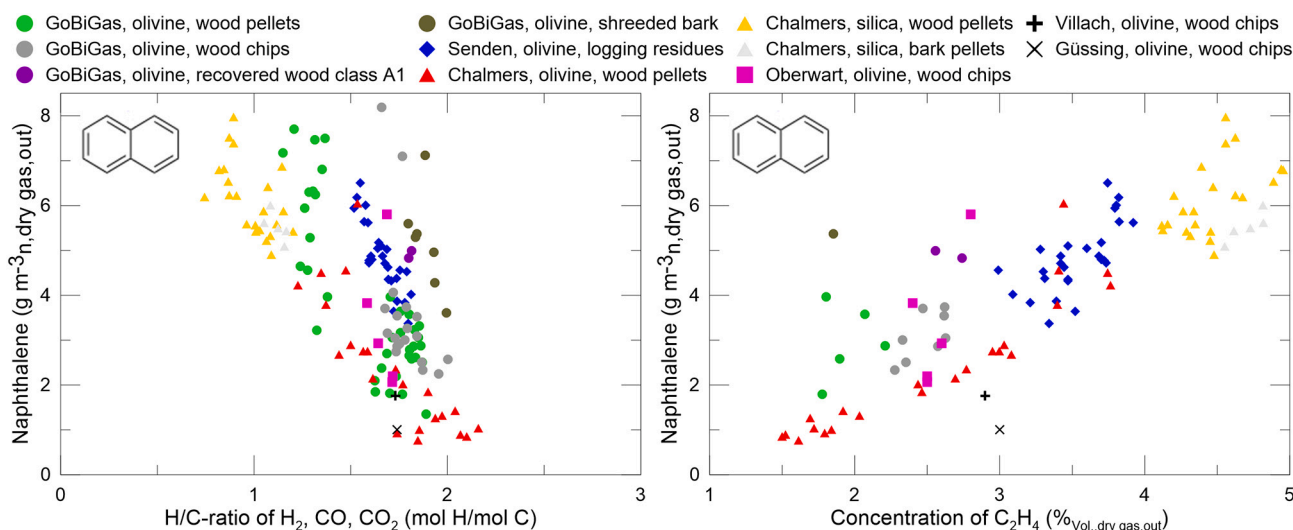


Fig. 10. Naphthalene concentration as a function of the H/C-ratio (left) and concentration of C₂H₄ in the dry gas (right).

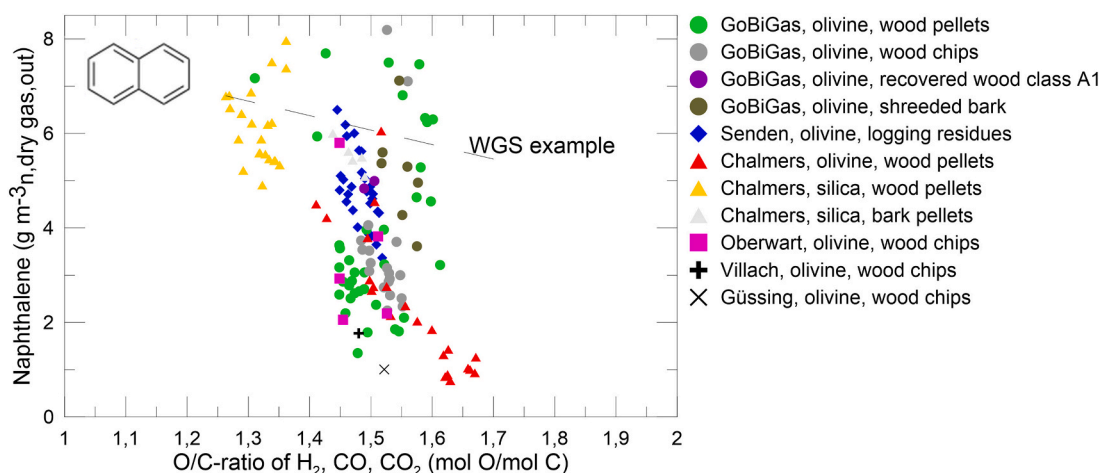


Fig. 11. Concentrations of naphthalene in the dry product gas, including an example of the potential impact of the WGS reaction on the concentration of naphthalene for the case with the highest concentration of CO, based on Eq. (2).

feeding screw based on the operational experience at the GoBiGas plant.

Correlations based on the concentration of CH₄ as an indicator of the activation level are less-sensitive to changes in the oxygen transport with the bed material, the use of purge gas, and potential leakage than are correlations based on the H/C-ratio and O/C-ratio. The concentration of CH₄ is also easier to measure online than that of C₂H₄. Therefore, the following analysis is based on using the CH₄ concentration as an indirect indicator of the level of bed activation.

Fig. 12 shows the concentrations of the tar components as a function of the CH₄ concentrations. The trend of lower concentrations of tar components with lower CH₄ concentrations seems to be generally valid for all the investigated cases. Fig. 12 indicates a segregation of the CH₄ concentrations based on the activation method applied. Weak activation based on the CH₄ concentrations (12%–15%_{vol,dry}) is observed for those cases in which silica sand or fresh olivine is used as the bed material. Moderate activation based on the CH₄ concentrations (9%–12%_{vol,dry}) is observed when olivine is used as the bed material and activated through the addition of calcium and/or fuel ash. Strong activation based on the CH₄ concentrations of (6%–9%_{vol,dry}) is observed for cases with olivine as the bed material and the addition of potassium or potassium and calcium, in addition to the fuel ash. Nevertheless, for a given CH₄ concentration there is a relatively wide range of possible concentrations of tar components, which reveals that it is possible to have high concentration of a specific tar compound even at strong activation levels. This is discussed further with the focus on pyrene, for which this feature is most apparent. The significant scatter in the data at a specific CH₄ concentration shows that for the purpose of controlling the activation level, and thereby the tar concentration, it is recommended to quantify during the commissioning of the gasifier a plant-specific correlation for each fuel and bed material that will be used.

The concentrations of pyrene in the product gas from the GoBiGas gasifier are in many cases significantly higher than those in other gasifiers when comparing cases with similar CH₄ concentrations. Note that the concentrations are different for different fuels, and that the scatter at a specific CH₄ concentration is high, however, for most cases the concentration of pyrene is significantly higher than that measured at other gasifiers with a similar CH₄ concentration, regardless of the fuel used at GoBiGas. The scatter indicates that the concentrations of pyrene, and probably those of other larger PAHs of group 5, are strongly affected by other parameters such as the temperature profile, mixing and the residence time. The data from GoBiGas with CH₄ concentration > 9% were acquired at the start-up of the plant, before potassium addition was initiated. At that point, the high concentrations

of large PAHs caused massive fouling in the downstream product gas cooler, forcing the plant to shut down after only a couple of hours.

This can be compared to the Senden plant where the operation commenced without significant fouling problems and continued for more than 2000 h even with an activation level that yielded a CH₄ concentration of around 10%. This was possible even though the gas was cooled to an even lower temperature as Senden than at the GoBiGas plant (Table 3). At the Chalmers plant, the concentrations of pyrene are also significantly lower than at the GoBiGas plant, albeit with a similar activation level. Even when using silica sand as a bed material that provides very weak activation, the concentrations of pyrene at the Chalmers plant are significantly lower than with the moderate activation of olivine at the GoBiGas plant. The scarce values reported from the plants in Oberwart and Villach are more in line with the results from the Senden and Chalmers plants. Thus, when designing the gas cooler, it is not sufficient to consider only the activation when specifying to what temperature the gas can be cooled without significant fouling.

The concentrations of heterogenic aromatic compounds (phenol and benzofuran), as well as of branched aromatic compounds (styrene and 2-methylnaphthalene) appear more segregated between different gasifiers than do the concentrations of saturated compounds. In most cases, the concentrations of these tar components are very low or even zero at GoBiGas, Oberwart, Güssing and Villach, while they exist at more relevant concentrations in the gas from the Senden and Chalmers plants.

To investigate further the cause of the scatter seen in Fig. 12, a number of univariate studies was selected and highlighted in Fig. 13. For these data-points, a single variable was varied, while keeping all the remaining variables as constant as possible (for a description and references related to these studies, see Table 6). The data-points in Figs. 12 and 13 are the same, although they highlight different aspects of the data. Where possible, the effect of an increase of the investigated parameter is illustrated with an arrow to simplify the reading of the plots.

The impact of bed activation has been studied at the Chalmers plant by starting the process with fresh olivine and conducting measurements on several occasions as the bed material ages and is activated, in one investigation by the fuel ash and in the other investigation by the addition of potassium. The trends for the data from the two investigations are in this context inseparable and are for simplicity illustrated here as a single correlation (red dots in Fig. 13). Note, however, that adding extra potassium significantly reduced the time for activation and a stronger activation level was eventually reached. All the components, with the exception of pyrene, show an almost linear correlation, while almost no change in the concentration of pyrene occurred during these investigations. This is a further indication that the concentrations of

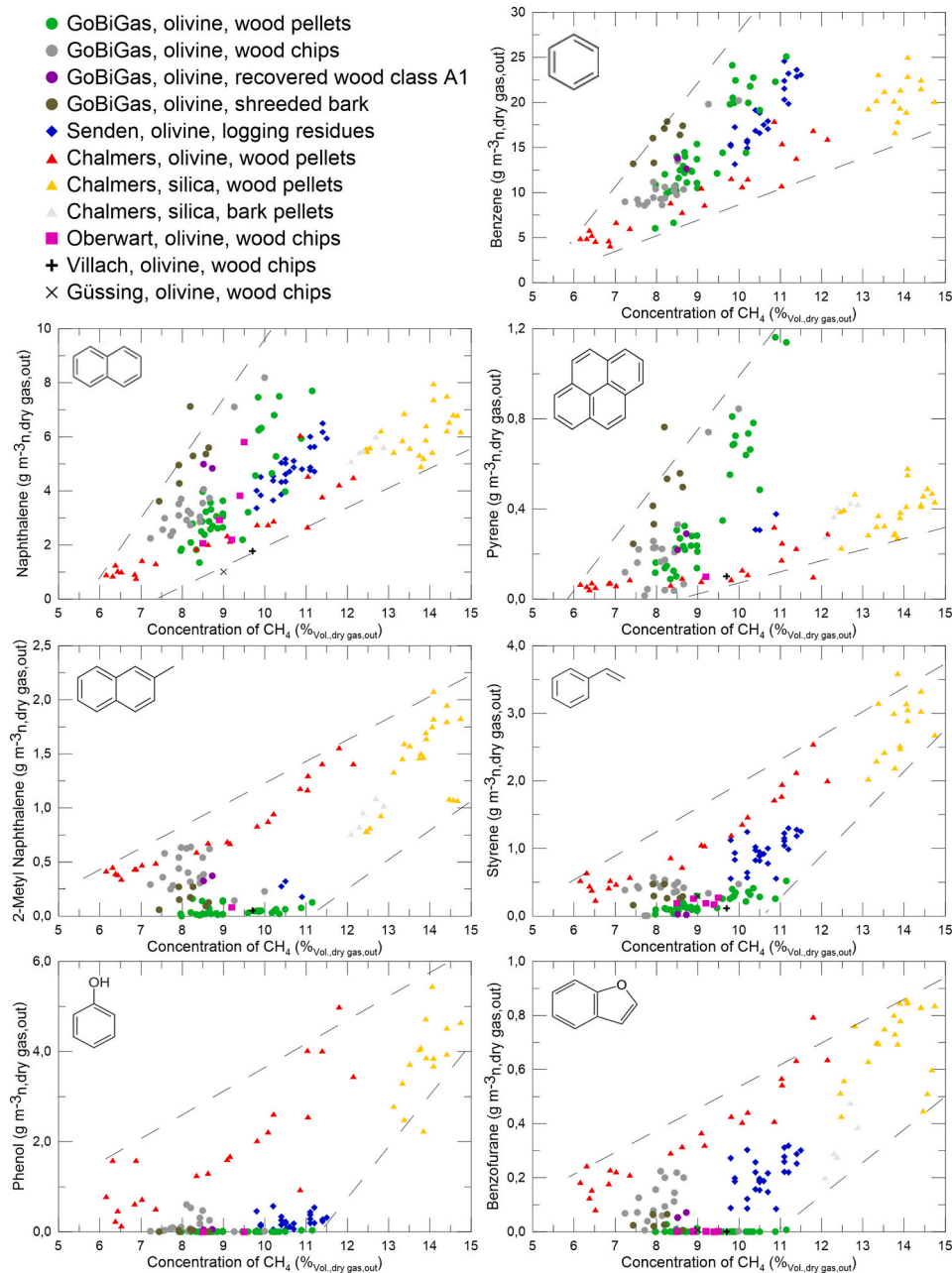


Fig. 12. Concentrations of tar components as a function of the concentrations of CH_4 in the dry product gas from the different DFB gasifiers. Dotted lines are arbitrary and included as a visual aid to indicate the range of data (they are not trend lines).

group 5 tar components are less affected by bed activation, as compared with the other tar components.

The bed temperature contributes significantly to the data scatter for those cases with moderate activation, as shown at both the Senden (*Bed temperature, Ca*, green dots in Fig. 13) and Chalmers (*Bed temperature, Ash*, yellow dots in Fig. 13) plants, where a change in temperature results in large changes in the concentrations of the tar components but only minor changes in the CH_4 concentration. Note that with a higher temperature, the concentrations of the mature tar components of groups 1, 3 and 5 increase, while the concentrations of the tar components in groups 2, 4 and 6 decrease. This is in line with the tendency to form more saturated components while forming fewer branched and oxygenated components at higher temperature, as previously described in the literature [44].

With a strong bed activation in the Chalmers gasifier (*Bed temperature, K*, purple dots in Fig. 13), there is no clear impact from a

change in the temperature, and the data scatter due to changes in the temperature are here lower at stronger levels of activation. The impact of temperature is further investigated in the next section in relation to process severity.

Part of the data scatter can be linked to the residence time in the reactor, which was investigated in the Chalmers gasifier using silica sand as the bed material (*Residence time*, orange dots in Fig. 13). An increased residence time for the gas (decreased GHSV) resulted in increases in the concentrations of naphthalene and pyrene, styrene, 2-methylnaphthalene and benzofuran, but not in the concentrations of benzene and phenol. The residence time was altered by simultaneously changing the feeding rates of the fuel and steam, so as to maintain a constant STF-ratio. Therefore, the fluidization and mixing of the fuel were altered, which complicated the analysis of the impact of the residence time. While no conclusion can be drawn from Fig. 13 itself, the impact of a changed GHSV is investigated in the following section.

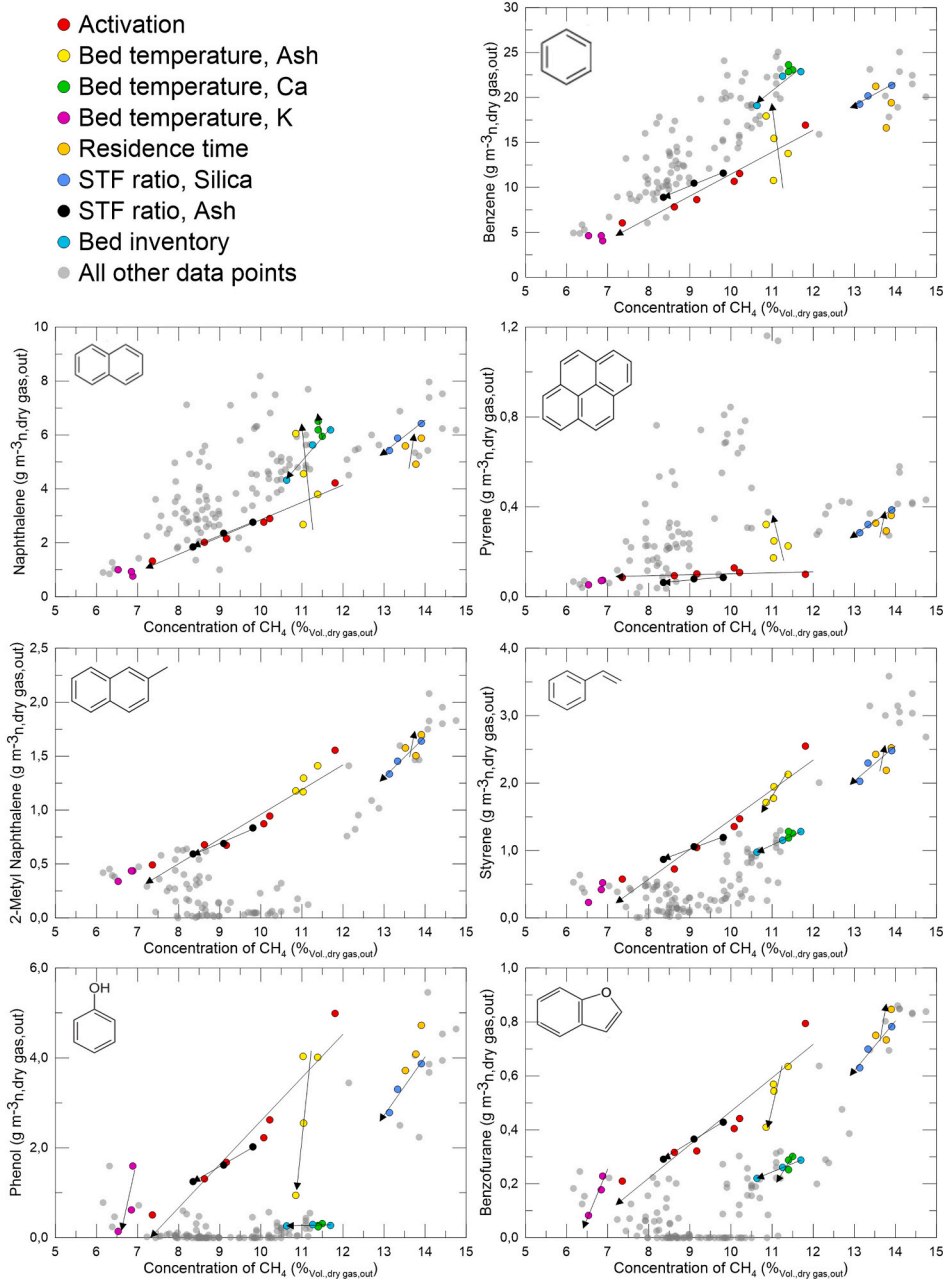


Fig. 13. Concentrations of benzene, naphthalene, and pyrene as a function of the concentrations of CH_4 in the dry gas. Univariate investigations listed in Table 6 are indicated by different colors, and the trends for the univariate studies are indicated with gray arrows pointing in the direction in which the values shift with an increase in the value of the specific variable.

When only the amount of steam was changed in the same study, so as to alter the STF-ratio (*STF ratio, Silica*, blue dots in Fig. 13) the effect was a reduction in both the tar and CH_4 concentrations with a higher STF-ratio. In a similar test, using olivine as the bed material in the Chalmers gasifier (*STF ratio, ash*, black dots in Fig. 13), similar but stronger impacts on the concentrations of both CH_4 and the tar components were seen. Changing the amount of steam used for fluidization has several effects, including a reduced residence time and dilution of the gas, which could limit the polymerization of the gas, although it also has a strong impact of the mixing of the solids and gas in the fluidized bed. A higher fluidization velocity increases the dispersion of both the bed material particles and fuel particles [48–50], which could increase contact between the active components and the primary tar components released from the biomass.

The bed material inventory was altered over a wide range at the

Senden plant (*Bed inventory*, cyan dots in Fig. 13), quantified as a pressure drop over the bed. An increased bed inventory confers an effect similar to that of increased activation, with a decrease in the concentrations of both CH_4 and tar components. In the Senden gasifier, the feedstock is always introduced into the fluidized bed close to the bottom of the reactor. Depending on how efficiently the bed is fluidized at the point where the fuel is introduced (e.g., the inclined wall at the Senden gasifier), the contacts between the volatiles and the bed particles are significantly affected. If the bed is well-fluidized the gas released due to drying and devolatilization and the strong vertical mixing in the FB will transport the particles rapidly to the bed surface, where the majority of the volatiles will be released [25]. For reference, it takes about 40 s to devolatilize a wood pellet in the FB [34] and even longer for a particle that is larger or has a higher moisture content. This is much longer than the expected time for the particles to travel to the

surface of the bed. This implies that feeding the fuel into a well fluidized region will have a limited impact on the gas-particle contact compared to on-bed feeding to the same region. Still, it has been shown that with a fluidization number in the range of 4–10, at least 40–60% of the volatiles come in contact with the bed material when the fuel is fed on top of the bed [17]. However, if the fluidization is poor the particles can be trapped, and due to the low level of mixing, the heat transfer will be significantly decreased and could yield a local decrease in temperature. It is not known how well the bed was fluidized at the point of fuel feeding and how the change of bed inventory affected the mixing at the Senden plant during this investigation.

In another investigation, additional fluidization nozzles were added to the inclined section at the fuel feed in the Senden plant [51], to ensure that the bed was well-fluidized in this area; this resulted in a significant reduction in the tar concentrations. The reconstruction of the plant at Senden proved that good fluidization in the bed area of the fuel feeding reduced the tar concentrations. Therefore, the design of the fuel feeding also affects the mixing, and it can be argued that by spreading the fuel over the bed the availability of the active components can be better maintained at all locations where the fuel is converted. Poor mixing can reduce the availability of active components, and given the volatile nature of potassium, it could even lead to local depletion of active potassium-containing components. In the Chalmers gasifier, the fuel was fed onto the surface of the bed via a downcomer, while in the other gasifiers the fuel was fed by a screw into the bubbling bed. With a well-fluidized bed, this will yield a very limited residence time in the bed compared to the time required for complete devolatilization. However, the difference between in-bed and on-bed fuel feeding has not been quantified in large-scale DFB gasifier, and a stronger level of bed activation and good gas quality have been achieved with both approaches. Regardless of the design of the fuel-feeding system, good mixing should be prioritized to increase the availability of active components to the volatiles leaving the fuel particles. With a well-fluidized bed at the fuel-feeding location, the design of the fuel feed can be focused on delivering high availability and low complexity, as well as efficient purge gas usage.

3.5. Process severity in the gasifier

The severity of a process is related to process parameters such as temperature, residence time (or GHSV), and mixing, which affect the main reactions of the process. As indicated by the PCA, only a fraction of the variance in the data can be attributed to these parameters and rather poor correlations can be expected. Some relevant information was, however, uncovered when plotting the tar concentrations as a function of the temperature as well as the GHSV based on the dry product gas out of the reactor. This is shown in Figs. 14 and 15, respectively. Tar data for some of the early cases from the GoBiGas plant that involved high tar concentrations are missing in the dataset.

Saturated tertiary tar components, of groups 1, 3 and 5, show a weak correlation to the temperature, while the levels of secondary and alkyl tertiary tar components, of groups 2, 4 and 6, tend to decrease at higher temperatures, especially when there is moderate-to-strong activation. While no general correlation between some of the tar species and the temperature was found in the present dataset, such correlations have been previously reported for specific units [6,7]. The results show that caution should be exercised when generalizing and applying these correlations to other gasifiers, especially when different bed materials, activation levels or fuels are used. To investigate the impact of the temperature on this type of process, one needs to keep constant in a stringent way all the other process parameters, especially the availability of catalytically active components, such as calcium and potassium. However, this might not be possible in large-scale units operating with a combination of bed material and ash that enables significant catalytic activity, such as olivine and biomass, as the temperature will also affect the mobility of the active components. With a

higher temperature, the partial pressure of potassium components in the gas phase increases in both the flue gas and the product gas. Thus, operating at a reduced temperature may increase the accumulation of potassium in the bed, thereby indirectly providing a lower tar concentration. At higher temperature the mobility of the potassium components increases and thereby loss of potassium increases. This loss should be compensated with makeup potassium to ensure a good control of the yield of tar.

At the GoBiGas plant, with a higher bed temperature, it was more challenging to start the gasifier without entailing a significant amount of fouling in the product gas cooler. Therefore, a bed temperature in the gasifier in the range of 800°–820 °C was used during start-up to minimize the risk of clogging the cooler during this period. At temperatures ≥ 870 °C, it was increasingly difficult to establish sufficient activation without clogging the cooler with tar or potassium-rich deposits [5]. This problem might be resolved with a different design of the product gas cooler or gasifier. Operation with a bed temperature as low as 760 °C was tested with good results at GoBiGas, and even lower temperatures have been tested at the Chalmers plant, revealing minor impacts on the concentrations of both the investigated tar components and main gas components when operating with strong activation.

The fouling risk with K-activation relates to the higher mobility of active K components compared to active Ca components. The high mobility of active K components means not only that they have strong catalytic activity, but that also there are significant losses of these components together with both the flue gas and product gas. Adding too much potassium risks causing fouling of the ash instead of tar reduction, so the addition needs to be balanced. While Ca-based components are less mobile and require a good gas-solids contact, they also help mitigate the risks for agglomeration and fouling of sticky ash components, such as potassium-silicate. Both Ca and K are always present in the fuel and, thereby, added to the process to some extent. The main difference between the activation methods relates to the additives added to the process. It has been shown that strong activation with very low tar concentrations can be achieved with K as the sole additive and Ca addition only via the fuel ash. However, it may be sensible to add some additional Ca, to limit the risks of agglomeration and formation of sticky ash components and to improve the utilization of the potassium through synergistic effects. This is especially true if the fuel ash is rich in silica or the fuel contains silica-rich contaminants, such as dirt or stones.

The dry GHSV out of the reactor can be varied by changing the rates of fuel feeding and steam addition (as illustrated in Fig. 9). However, it also depends on the reactor volume and, therefore, varies over a wide range for the investigated gasifiers. Fig. 15 indicates that the dry GHSV has a weak correlation to the general dataset, with a tendency towards lower concentrations at higher dry GHSV, and thus a lower residence time if the steam concentration remains the same. As the activation of the bed and the bed material inventory have strong impacts on the production of dry gas, it is difficult to decouple these effects based on the current data. Furthermore, a reliable measurement of the concentration of steam is required to analyze the true GHSV and not only the dry GHSV.

Fig. 15 indicates that there are discrepancies in the results between different reactors and fuels. For a specific gasifier with a specific fuel there is, however, an evident correlation between the concentrations of the tar components and the GHSV based on the dry product gas. These trends indicate that a higher dry GHSV yields lower concentrations of the investigated components. It is not known whether this is due to changes in the activation level or yield of dry gas components (dilution) or in fact is a consequence of a change in the residence time for the tar components.

The investigations conducted in the Chalmers gasifier with silica sand as the bed material indicate an increased concentration of tertiary tar with a higher residence time (range, 4.0–5.5 s) and, thereby, a lower dry GHSV out [8]. By applying silica sand as bed material, the

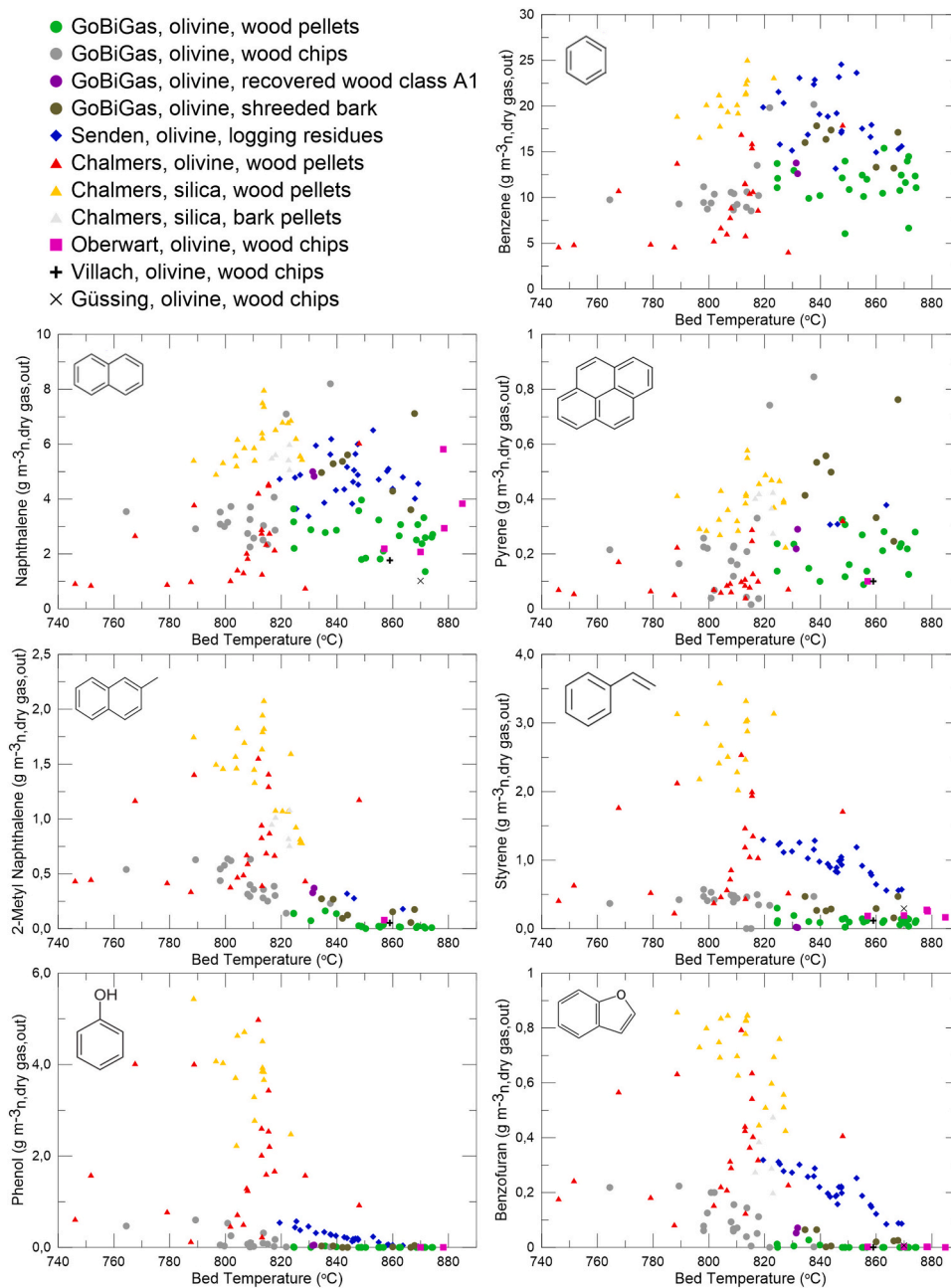


Fig. 14. Concentrations of tar components as a function of the bed temperature in different DFB gasifiers operated with various bed material and feedstocks.

uncertainties coupled to the active ash components are minimized, as the silica sand binds the active ash components in a non-active state. However, the change in residence time achieved by changing both the fuel feed and the fluidization steam, while maintaining constant the STF-ratio, will also affect the mixing in the gasifier, such that the effect of the residence time still cannot be completely decoupled. Nevertheless, as discussed by Berdugo [17], it can be argued that a prolonged residence time will have limited effects on the slow steam cracking and reforming reaction, while having a stronger impact on the undesired and faster growth of tar components through polymerization. This notion is neither confirmed nor contradicted by the data in the present work.

Generally, the bed temperature in the gasifier has a limited impact on the gas quality compared to the level of bed activation. Higher severity in terms of higher temperature and longer residence time is expected to lead to further polymerization of tar components, yielding higher concentrations of large tar components with high dew-points.

Therefore, a high residence time at high temperature for the volatiles should be avoided. The temperature in the bed affects a range of parameters, including the activation of the bed material, risk of agglomeration, heat demand of the process, char conversion rate, composition of the tar, and total yield of tar. The optimal bed temperature for operation of a gasifier will be a tradeoff between these parameters and can be expected to be plant-specific, depending on the level of heat recovery, gas conditioning technology etc. For the gasifiers included here, a bed temperature in the range of 800–870 °C has proven to be viable from the operational perspective. A rule of thumb for dry biomass is that as long as you need to recirculate some of the produced gas to the combustion side, one can reduce the temperature to decrease the heat demand of the process, which gives a higher cold gas efficiency. A lower bed temperature also reduces the rate of conversion of char, so that more char is transported to the combustion side of the process, further reducing the need for recirculation of the gas.

The mixing processes in the investigated reactors cannot be

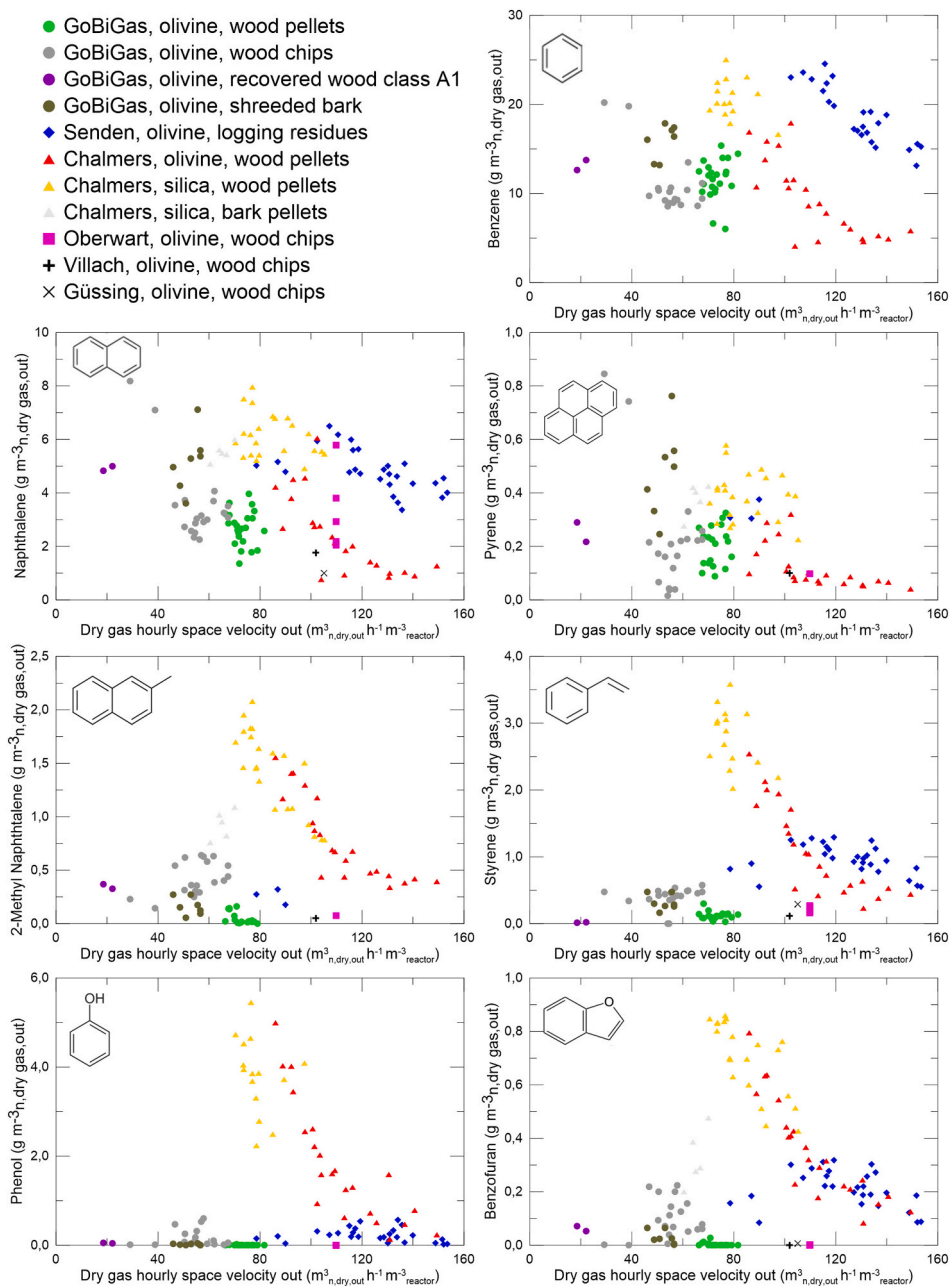


Fig. 15. Concentrations of tar components as a function of the dry gas hourly space velocity (GHSV) out of different DFB gasifiers operated with various bd material and feedstocks.

described in detail due to the difficulties to quantify the gas velocity profile and a representative particle size. Therefore, a couple of available parameters known to influence the mixing have been quantified. These are the amount of fluidization steam per area unit of the fluidized section and the freeboard, respectively, and the amount of steam per volume unit of dry product gas. Owing to the significant difference in shape between the Chalmers gasifier and the other gasifiers, there is a significant difference in the amount of steam per square meter of fluidized bed section (see Table 3). For the freeboard section, this ratio is more similar. The range of values for steam-to-dry gas are rather similar for all the datapoints, with the exception of those from the GoBiGas plant operated with recovered wood as the fuel; during those tests, the values for steam-to-dry product gas were very low due to restrictions imposed on the fuel feeding. No general trends related to these parameters are identified based on the current data, as the scatter caused by other parameters are substantial and the ranges of these parameters in a

specific gasifier are limited. However, univariate investigations, focusing on a much narrower range, have shown that increased fluidization can reduce slightly the yield of tar [34], although the impact is dwarfed by variations in other operational parameters, as shown in the present study.

The level of activation required at a specific plant will be dictated by the maturity of the tar components in the product gas as well as the downstream equipment, especially if the product gas is cooled down for heat recovery before being cleansed of tar. Cooling the product gas to < 200 °C in gas-fired types of coolers (as is the case in most of the investigated plants), requires a certain level of activation to limit fouling by the tar. Furthermore, results indicate that the severity of the gasification process can have a strong impact on the maturity of the tar and the yields of tar components that have high dew-points. In particular, in the GoBiGas gasifier, the yield of the large tar component pyrene was significantly higher than in the other gasifiers, and

experience has shown that a low concentration of CH₄ (about 8.5%) is required to avoid fouling. This could only be achieved by continuously adding potassium to the process. In contrast, the gasifier in Senden can be operated with a CH₄ concentration of about 10%, even with a lower temperature in the gas cooling section, such that extensive fouling and sufficient activation can be achieved without adding extra potassium.

4. Conclusions

The results show that despite differences in design, operational strategies, and measurement methods applied in biomass steam gasifiers, the availability of active components in the reaction environment is the parameter with the strongest impact on the quality of the product gas. The recommendations for the design and operation of steam gasifiers based on the current experience at large scale are:

- A balance of catalytically active compound is crucial to control the gas quality, which can be attained with the use of additives and a correct handling of ash streams. In the investigated DFB units, the catalytic activity is attained in-situ by the interaction of the olivine bed with the active compounds, where the activation process can be accelerated by the use of additives. The consumption of fresh bed material and additives can be limited by retrieving and recycling the used bed material from both the flue gas separation and bottom ash separation.
- For automated control of the activation level by feeding additives, a correlation between CH₄ concentration in the flue gas and activity of the bed material can be established. To minimize uncertainties, it is recommended that the correlation is plant specific. A preliminary set-point for the CH₄ concentration can be established based on the data presented here.
- The gasification temperature has a limited impact on the gas quality compared to the impact of active compounds. The optimal gasification temperature in a large steam gasifier is plant specific as it is the result of a tradeoff between availability of catalytic compounds, heat demand of the process, char conversion rate, composition of the tar, total yield of tar, and in the case of fluidized bed gasifiers also the risk of agglomeration.
- The key to a good conversion is to ensure access of the volatiles to the active components. In DFB gasifiers this can be achieved with a well-fluidized bed. Both in-bed and on-bed fuel feeding can result in low tar yields

Finally, the data from the six large-scale DFB gasifiers show a relatively low sensitivity of the gas composition to the size, design, operation and control strategies chosen, which indicates that the technology is robust and can be upscaled. Thus, the gas and tar compositions presented here constitute relevant reference data for large scale steam gasification of biomass.

CRediT authorship contribution statement

Anton Larsson: conceptualization, methodology, validation, formal analysis, investigations, data curation, writing-original draft, visualization, project administration

Matthias Kuba: funding acquisition, project administration, investigation, validation, data curation, writing-review & editing

Teresa Berdugo Vilches: conceptualization, methodology, investigation, validation, data curation, writing-review and editing

Martin Seemann: funding acquisition, project administration, writing-review & editing

Hermann Hofbauer: funding acquisition, project administration, writing-review & editing

Henrik Thunman: funding acquisition, project administration, writing-review & editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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