

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

**Strategies for controlling solid biomass conversion in dual fluidized bed  
gasifiers**

Teresa Berdugo Vilches

Department of Energy and Environment

CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2016

Strategies for controlling solid biomass conversion in dual fluidized bed  
gasifiers

© Teresa Berdugo Vilches 2016

Department of Energy and Environment  
Division of Energy Technology

Chalmers University of Technology  
SE-412 96 Gothenburg  
Sweden  
Telephone + 46 (0)31-772 1000

Printed in Sweden  
Chalmers Reproservice  
Göteborg 2016

# **Strategies for controlling solid biomass conversion in dual fluidized bed gasifiers**

Teresa Berdugo Vilches  
Division of Energy Technology  
Department of Energy and Environment  
Chalmers University of Technology  
SE-412 96 Gothenburg (Sweden)

## **Abstract**

In the chemical industry, Synthesis Gas (syngas) has been traditionally produced by steam reforming of natural gas and naphtha. Steam gasification of biomass offers an alternative route for the production of syngas from renewable sources. However, the product of biomass gasification cannot be used directly in most applications, as it contains impurities, such as tar species. Tar, which is the Achilles heel of the biomass gasification technology, is a complex mixture of hydrocarbons, which can condensate at temperatures as high as 300°C, causing clogging of pipes and coolers, deactivating downstream catalysts, and forcing unscheduled shut-downs of the whole process.

Gas cleaning and upgrading techniques, as well as methods for controlling the formation of tar are required to limit the tar concentration to acceptable levels. Numerous investigations of this topic have led to the merging of the fields of steam reforming and gasification, whereby catalytic materials are placed inside the gasifier with the goal of steam reforming the undesirable tar species and converting them into valuable syngas. The feasibility of integrating gasification and catalytic steam reforming has been confirmed in several pilot and demonstration plants, with promising results. The preferred technology is indirect gasification in a dual fluidized bed (DFB) reactor, as it enables hosting of the catalyst in the steam gasifier.

The levels of tar in biomass gasification remain high, and there is a lack of understanding as to how to control efficiently fuel conversion in general, and tar formation in particular. Efforts to reduce the load of tar have ranged from modifying the gasifier design to testing different catalytic materials, passing through optimization of operating conditions (e.g., temperature, steam-to-fuel ratio). However, previous investigations have mainly focused on assessing the marginal improvement in product gas quality that occurs after a modification in the operation. This work aims instead at identifying the most effective measures to control fuel conversion in DFB gasifiers, with the ambition of contributing to the rational operation and design of the gasifier.

In this work, fluid-dynamics and chemical aspects of fuel conversion are explored experimentally under conditions relevant to industrial steam gasifiers. It is concluded that the activity of the catalyst is the primary tool to control both tar and char conversion, whereas the fluid dynamics of the bed plays a secondary role. Once the bed is well-fluidized, further

optimization of the gasifier design results in relatively low improvement in terms of tar conversion, as compared to the benefits of using active bed materials. Accordingly, to improve the reliability of the biomass-to-syngas process, research efforts should be directed to understand catalyst activation, the functioning of the catalyst, and the mechanism underlying catalytic decomposition of tar.

*Keywords:* dual fluidized bed, *in situ* gas upgrading, steam reforming, tar removal, char gasification, segregation, operating conditions, olivine, ilmenite, bauxite, feldspar.

## List of Publications included in the thesis

---

- I. Teresa Berdugo Vilches, Henrik Thunman. Experimental Investigation of Volatiles-Bed Contact in a 2-4 MWth Bubbling Bed Reactor of a Dual Fluidized Bed Gasifier. *Energy & Fuels*, 2015, 29, 6456-6464.
- II. Erik Sette, Teresa Berdugo Vilches, David Pallarès, Filip Johnsson. Measuring fuel mixing under industrial fluidized-bed conditions – A camera-probe based fuel tracking system. *Applied Energy*, 2015, 163, 304–312
- III. Mikael Israelsson, Teresa Berdugo Vilches, Henrik Thunman. Conversion of Condensable Hydrocarbons in a Dual Fluidized Bed Biomass Gasifier. *Energy & Fuels*, 2015, 29, 6455-6575.
- IV. Teresa Berdugo Vilches, Jelena Marinkovic, Martin Seemann, Henrik Thunman. Comparing active bed materials in a dual fluidized bed biomass gasifier: olivine, bauxite, quartz-sand and ilmenite. *Energy Fuels*, 2016, 30, 4848-4857.
- V. Teresa Berdugo Vilches, Henrik Thunman. Impact of oxygen transport on char conversion in dual fluidized bed systems. Conference article, Nordic Flame Days, Copenhagen, 2015.
- VI. Nicolas Berguerand, Jelena Marinkovic, Teresa Berdugo Vilches, Henrik Thunman. Use of alkali-feldspar as bed material for upgrading a biomass-derived producer gas from a gasifier. *Chemical Engineering Journal*, 2016, 295, 80-91.

Teresa Berdugo Vilches is the principal author of Papers I, IV, and V. Erik Sette is the main author of Paper II, and he was responsible for the development of the computational methods applied to fuel tracking. Teresa Berdugo Vilches contributed with the operation of the gasifier, discussions, and editing of this paper. Mikael Israelsson and Nicolas Berguerand are the principal authors of Papers III and VI, respectively. Teresa Berdugo Vilches contributed with experimental work, evaluation of experimental data, discussions, and editing of these papers. Professor Henrik Thunman is the principal academic supervisor and has contributed with ideas and discussions to all the papers, as well as the editing of Paper I and Papers III-VI.

## **Publications not included in the thesis**

---

- Teresa Berdugo Vilches, Erik Sette, Henrik Thunman. Behavior of Biomass Particles in a Large Scale (2–4MWth) Bubbling Bed Reactor. Conference paper, Computational Methods in Multiphase Flow VIII, Valencia 2015.

# Acknowledgments

---

I would like to express my most sincere gratitude to my main academic supervisor, Prof. Henrik Thunman, for the opportunity to pursue the PhD degree, for coaching me in the art of research, and for high-quality and efficient supervision. Thanks to Dr. Fredrik Lind and Asst. Prof. Martin Seemann for always being eager to discuss, for your support during experiments, and for your inspiring attitude towards research. Thanks also to Asst. Prof. Nicolas Berguerand for first introducing me to the experimental work.

To research engineers Jessica Bohwalli, Johannes Öhlin, and Rustan Marberg: many thanks for your support with your technical expertise during the long days of experiments, for your patience with my Swedish language, and for being outstanding people. Thanks to the operating staff at Akademiska Hus: Rikard, Petrus, Roban and Mikael, for operating the boiler beyond the comfort zone, and for wearing a smile before 6 am!

I want to give special thanks to my co-authors. To Jelena Marinkovic, because you were my mentor at the beginning of my PhD, for your exceptional help in running experiments, and for the enriching discussions about research. To Mikael Israelsson, for closing the carbon balance (which made my PhD life easier :-D), for sharing with me all the mysteries of *SPA* and *Inferno*, and because working with you is fun. To Erik Sette, for the long discussions about mixing, for mastering the ‘magic’ of Matlab, and, of course, for the glasses of cava. To the rest of the gasification crew (Alberto, Anton, Huong, Angelica...), thanks for creating such a friendly and stimulating environment for developing new ideas.

Finally, to my parents, Rafael and María Jesús, for your unconditional support despite the 3260 km between us. To my beloved Alex, for always being there and for encouraging me to dare to aim high.

*Teresa Berdugo Vilches, Göteborg 2016*





# Table of Contents

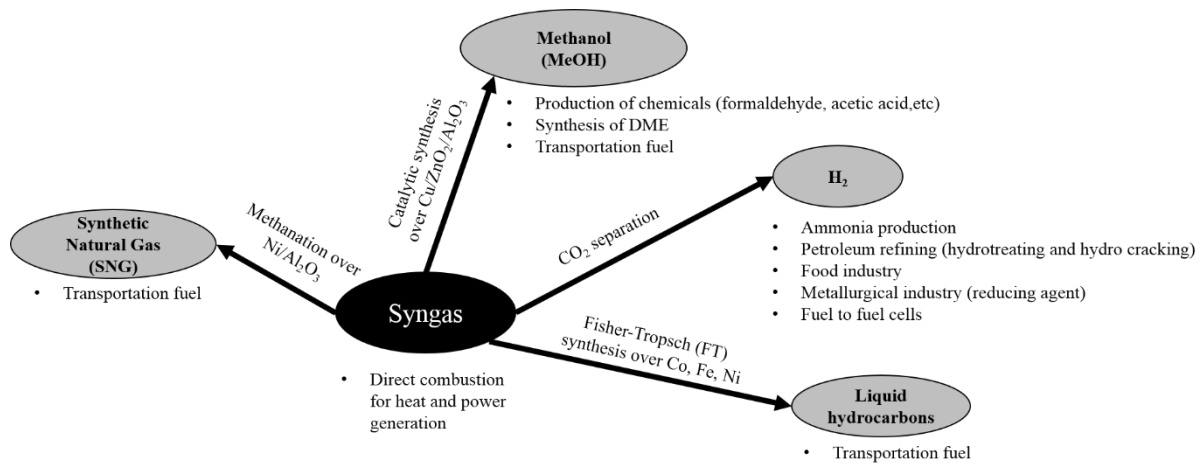
---

<b>List of Publications included in the thesis .....</b>	<b>iii</b>
<b>Publications not included in the thesis .....</b>	<b>iv</b>
<b>Acknowledgments .....</b>	<b>v</b>
<b>Table of Contents .....</b>	<b>vii</b>
<b>1 - Introduction .....</b>	<b>2</b>
1.1 Catalytic route from biomass to syngas .....	3
1.2 Indirect Gasification .....	5
1.3 Control of biomass conversion in the DFB gasifier .....	7
1.4 Aim and scope .....	8
<b>2 - Fluid-dynamics aspects of fuel conversion .....</b>	<b>10</b>
2.1 Vertical mixing and volatiles-bed contacts .....	10
2.2 Horizontal mixing and residence time of the fuel particles .....	10
2.1 Research approach .....	11
<b>3 - Chemical aspects of fuel conversion .....</b>	<b>14</b>
3.1 Temperature and steam-to-fuel ratio (S/F) .....	14
3.2 Catalytic bed materials .....	14
3.1 Impact of ash on catalyst activity .....	15
3.2 Flows of biomass ash in DFB gasifiers .....	16
3.3 Oxygen carriers .....	17
3.4 Research approach .....	18
<b>4 - Experimental .....</b>	<b>20</b>
4.1 Gasifier .....	20
4.1.1 Camera probe .....	21
4.1.2 Gas analysis .....	21
4.2 Downstream fluidized bed reformer .....	22
4.3 Bed materials tested .....	23
<b>5 - Results and discussion .....</b>	<b>26</b>
5.1 Vertical and horizontal mixing of the fuel .....	26
5.2 Operating conditions and active materials .....	27
5.3 General discussion .....	33
<b>6 - Conclusions .....</b>	<b>36</b>
<b>7 - Future work .....</b>	<b>38</b>

<b>8 - References.....</b>	<b>40</b>
----------------------------	-----------

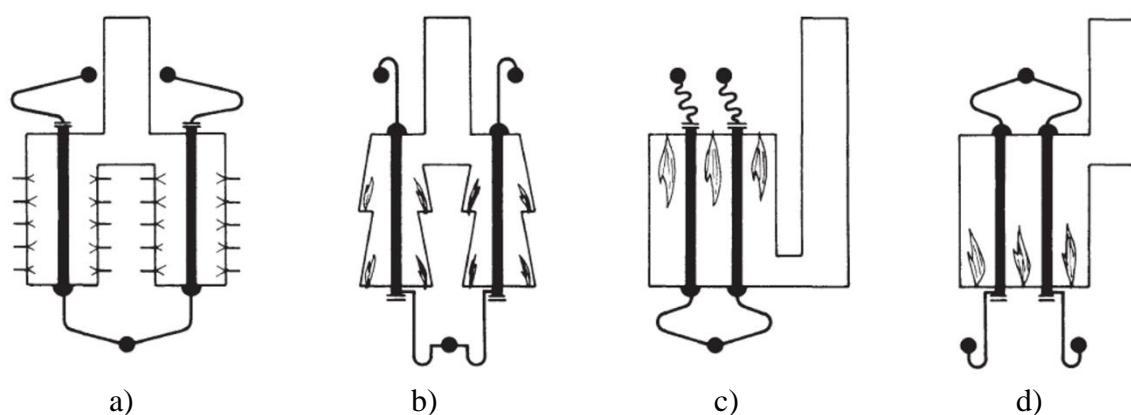
# 1 - Introduction

Steam reforming refers to the conversion of a carbon containing feedstock into a mixture of CO, CO<sub>2</sub>, and H<sub>2</sub>. The reactions take place in steam environment with the assistance of a catalyst. The product gas is commonly known as Synthesis Gas (syngas), which is a key intermediate in the chemical and refinery industries, e.g., for the production of methanol, DME, Fisher-Tropsch liquids, and synthetic natural gas (SNG). More importantly, steam reforming is a major actor in the production of hydrogen, which is a reactant in the production of ammonia, and in the hydrotreatment and hydrocracking of naphtha in the petroleum industry [1]. Figure 1 summarizes the current and potential applications of syngas and its derivate products.



**Figure 1.** Applications of syngas and its derivate products.

Nowadays, steam reforming is a well-established technology. The most commonly used design is the tubular reactor, which consists of a set of tubes (40–400) hosted inside a furnace [2]. The particular placement of the burners and the tubes varies according to manufacturer; Fig. 2 summarizes the typical reformer configurations. A steam reformer functions simultaneously as an energy converter and catalytic reactor, as both chemical reactions and heat production occur in the same unit. The carbonaceous feedstock (e.g., natural gas) is reformed inside the tubes, which accommodate a fixed bed of catalyst. The steam-reforming reactions are endothermic, with the heat required for the reactions being provided by the combustion of process gas (or an auxiliary fuel) in the furnace. This combustion takes place outside the reformer tubes, and the released heat is transferred to the reformer reactor *via* radiation and convection to the walls of the tubes [3].

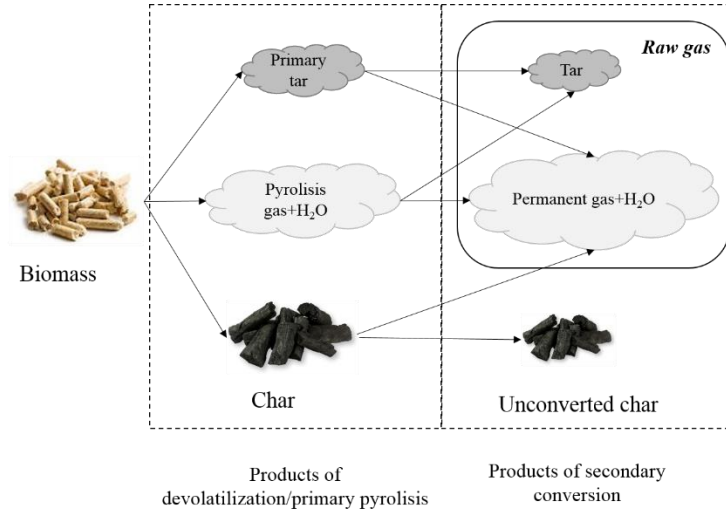


**Figure 2.** Reformer furnace configurations: a) side-fired; b) terrace-wall; c) top-fired; and d) bottom-fired. Adopted from [2].

Since the first steam reformer was constructed in the 1930s, natural gas has been the preferred feedstock for the production of syngas, with naphtha being also used later on [2]. As an alternative to fossil fuels, biomass may be used as the raw material, enabling the production of biofuels and biochemicals through chemical routes similar to those used for processing syngas of fossil origin. However, the use of biomass in catalytic processes is technically challenging, as it involves the use of: (1) a solid fuel, which is (2) rich in volatile matter, and (3) contains impurities such as sulfur, tar, and alkali species. The latter are known to poison commercial steam reformer catalysts [4, 5]. This thesis deals with the catalytic production of syngas using woody biomass as an alternative to the traditional steam reforming of fossil fuels.

## 1.1 Catalytic route from biomass to syngas

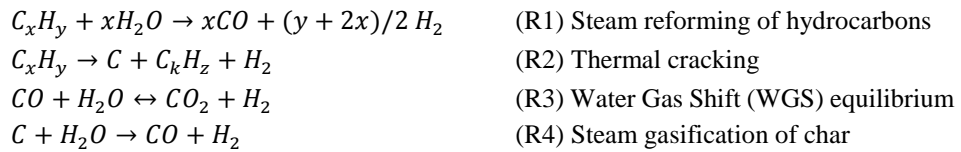
The production of syngas from solid biomass frequently involves a gasification-based process in which the solid fuel is converted into a mixture of gases (i.e., raw gas) by means of heat and a gasification agent, such as  $H_2O$ . A schematic of the conversion process is presented in Fig.3, and the relevant reactions that occur at atmospheric steam gasification conditions are listed in Table 1.



**Figure 3.** Products of primary pyrolysis and secondary conversion reactions during the thermochemical conversion of biomass in a steam environment.

For volatiles-rich fuels, such as the woody biomass used in this work, a major fraction of the biomass (86%–84% w/w) becomes a mixture of gases already during the primary pyrolysis step. The primary pyrolysis gas and the tar species undergo secondary conversion reactions, which increase the production of syngas species through R1–R3. The remaining solid char, which constitutes 16%–20% w/w of the parent fuel, can further contribute to the production of CO and H<sub>2</sub> through the steam gasification reaction (R4). However, the contribution of the char gasification to the production of gas is modest, as the yield of char is significantly lower than the yield of volatiles. Moreover, the rate of char gasification is slow (e.g., >15 min for wood pellets [6]), as compared to that of devolatilization (e.g., <30–40 s for wood pellets [7]), and this also favors the production of volatiles-derived gases at limited residence times in industrial reactors.

**Table 1.** Important reactions of biomass products in a steam environment under atmospheric pressure.

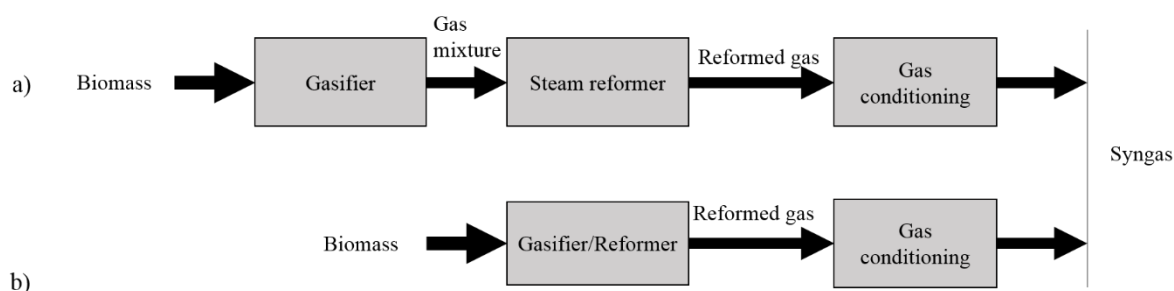


The resulting mixture of gases may contain more than 200 different hydrocarbon species [8], including problematic tar compounds. Biomass-derived tar has attracted considerable attention in the field of gasification, as it is considered to be the main technical hindrance for the biomass gasification technology. Tar condenses at temperatures as high as 300°–400°C, causing the clogging of pipes and coolers, as well as the deactivation of downstream catalysts in the synthetic processes [9]. The uncontrolled production of condensable species may lead to unplanned shut-downs of the plant, thereby restricting the availability of the process. Apart from causing operational difficulties for the biomass gasification plant, the concentration of condensable species in the raw gas limits the eventual application; some of the reported limits are listed in Table 2.

**Table 2. Reported tar limits for various applications. Compiled from [9, 10].**

Application	Upper limit for tar
Direct combustion	No limit specified
Gas turbine	<5 mg/Nm <sup>3</sup>
Internal combustion engines	<100 mg/Nm <sup>3</sup>
Fisher-Tropsch synthesis	<1 ppmv
Methanol synthesis over CuO/ZnO	<0.1 mg/Nm <sup>3</sup>
Pipeline transport (compressors)	50–500 mg/Nm <sup>3</sup>

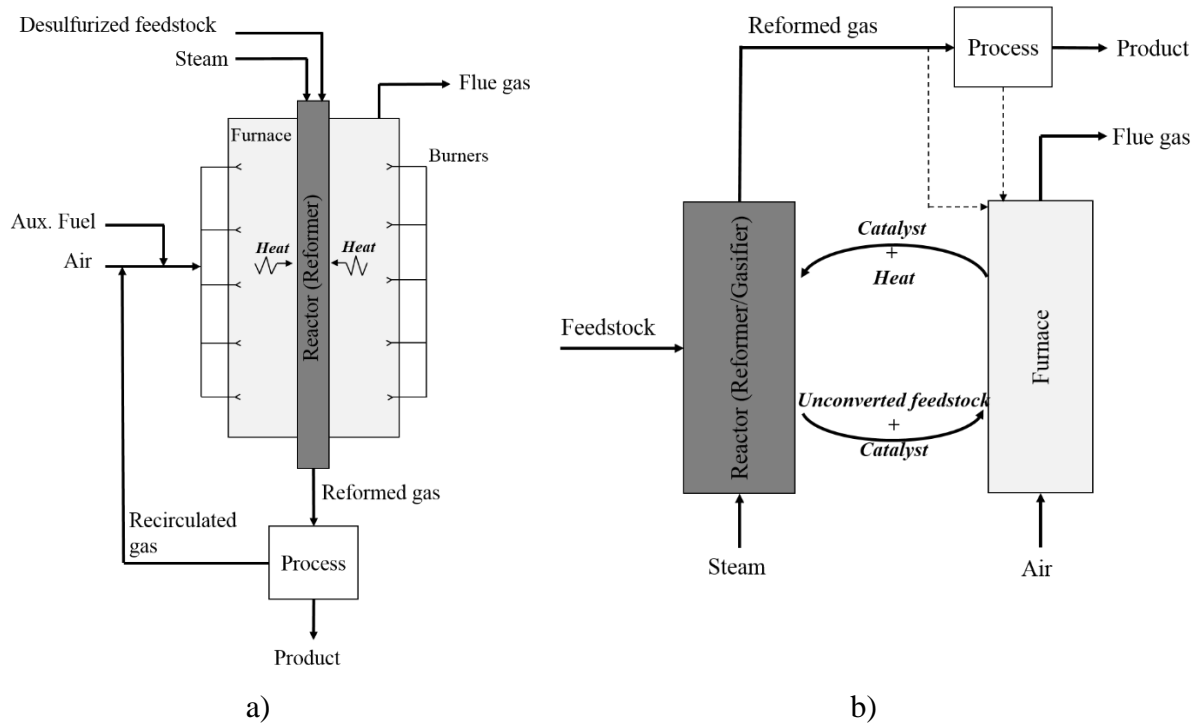
Ideally, all hydrocarbons should be converted to valuable syngas, and/or the condensable hydrocarbons should be converted to acceptable levels by, for example, catalytic steam reforming. As shown in Fig.4, steam reforming can be accomplished in a catalytic downstream reformer (secondary measures) or in a gasifier (*in situ* or primary measures) [11]. In the *in situ* approach, a steam reforming catalyst is located inside the gasifier. This combination of gasifier and steam reformer in the same reactor volume can be obtained in indirect gasification, which is the process investigated in this work. The concept has been demonstrated previously in, for example, the GoBiGas plant in Gothenburg [12] and the Güssing gasifier [13]. The main advantage that the *in situ* approach has over the downstream reformer is that it can simplify the plant layout by decreasing the number of process steps.



**Figure 4.** Simplified process schemes for catalytic production of syngas from biomass, involving: a) devolatilization followed by downstream reforming of volatiles; and b) *in situ* devolatilization and steam reforming.

## 1.2 Indirect Gasification

Indirect gasification is realized in a dual fluidized bed (DFB) reactor, as shown schematically in Fig.5b. In general, a DFB gasifier consists of two interconnected fluidized bed vessels with a hot bed material (or catalyst) circulating between the vessels. The vessels are separated by Loop Seals (LS), which enable the flow of bed material while preventing any mixing of the two gas environments [14]. The functioning of an indirect gasifier (IG) is similar to that of a typical tubular steam reformer, as they both operate as both a chemical reactor and energy converter. The similarities between the reactors are highlighted in Fig.5, and their main features are summarized in Table 3.



**Figure 5.** Schematic of: a) a tubular reformer; and b) a dual fluidized bed gasifier.

In an IG, the steam reforming of hydrocarbons takes place in one of the vessels (darker box in Fig.5b), which is the counterpart of the reformer tubes in a tubular steam reformer. The unconverted feedstock, which is mainly char, is transported by the bed material to the furnace (lighter box in Fig.5b), where it is combusted. A major difference between the steam reformer and the IG is the way in which the heat generated in the furnace is transported to the reforming reactor. In the classical tube reactor, the heat is transferred through the walls of the tubes [1], whereas in the IG, the heat is transported by the hot bed material (i.e., the catalytic bed) [14].

An operational advantage that the DFB configuration has over the classic tubular reformer is that the catalyst (i.e., the bed material) can be regenerated continuously from carbon deposits, as the carbon deposits on the catalyst surface will be burnt off in the furnace. Carbon formation is a challenge for commercial steam reforming (Ni-based) catalysts, as it reduces catalyst performance, necessitating eventual replacement of the catalyst [15].

**Table 3.** Comparison of the basic features of the tubular steam reformer and the DFB indirect gasifier.

Vessel	Characteristic	Tubular Steam Reformer	DFB Indirect Gasifier
Reactor	Reactions	Steam reforming	Devolatilization Steam reforming Char gasification
	Catalyst bed	Fixed Bed	Fluidized Bed
	Feedstock Product	Gas/Liquid feedstocks Reformed gas	Solid/Gas/liquid feedstocks Reformed gas
Furnace	Reactions	Combustion	Combustion Regeneration of catalyst
	Heat transfer to reformer	Radiation/convection to the wall of the reformer tubes	Radiation/convection from the hot bed material to the reactor environment
	Fuel	Recirculated process gas Auxiliary fuel/feedstock	Unconverted char from the reactor Recirculated process gas Auxiliary fuel/feedstock

### 1.3 Control of biomass conversion in the DFB gasifier

The gasifier is at the core of the biomass-to-syngas process, and its performance influences: (1) the efficiency of syngas production; (2) the extents of the gas cleaning and upgrading steps; (3) the types and yields of byproducts; and most importantly, (4) the continuity of the entire process. Accordingly, it is crucial to identify the main factors that govern the conversion of biomass inside the gasifier, so as to ensure the long-term availability of the process and the controlled production of syngas and byproducts.

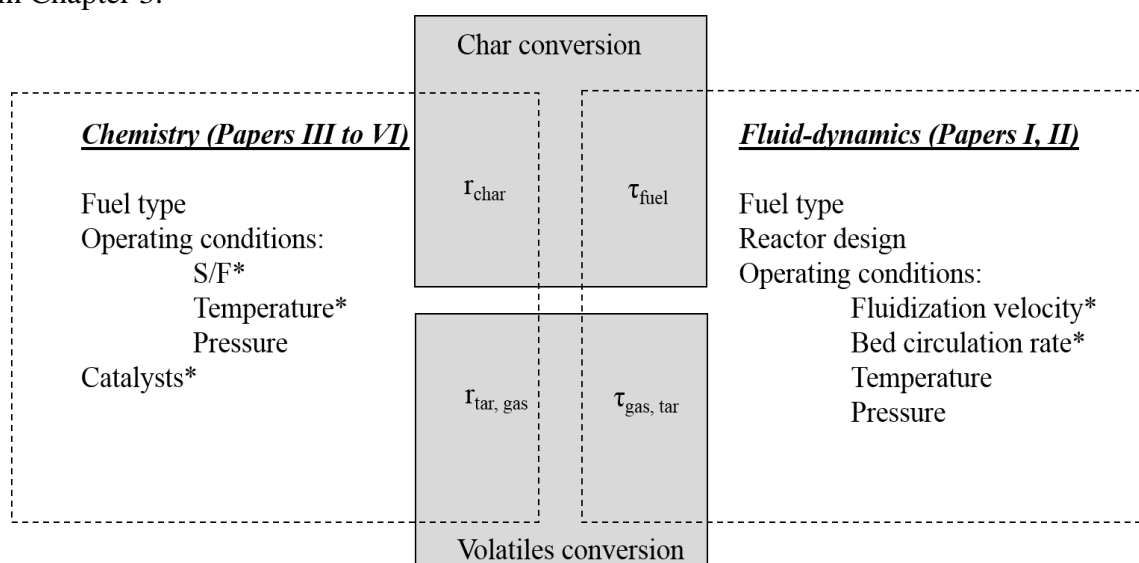
The degree of conversion of biomass into valuable syngas in a DFB indirect gasifier depends on a combination of the fluid-dynamics and the chemical features within the gasification/reformer reactor. Hereinafter, the gasifier/reformer will be referred to simply as the ‘gasifier’, although steam reforming is an important and desirable part of the process, as previously discussed. Figure 6 summarizes the parameters that affect gasifier performance, as well as their relationships to biomass conversion. The asterisks in the figure indicate those parameters that have been investigated in the present work.

**Fluid dynamics.** The fluid dynamics of the fluidized bed are reactor-dependent and they govern the effective time for reactions ( $\tau$ ): (1) the contact time between volatiles species, and the catalytic bed material; and (2) the residence time of the fuel particles in the reactor. Fluid dynamics can be described in terms of the mixing pattern of the fuel particles in the bed, which is determined by the gasifier design parameters (e.g., shape [16], fuel feeding position [17]),



the physical properties of the fuel (e.g., density, particle size [18]), and the operational conditions (e.g., fluidization velocity [19]). These aspects are described in Chapter 2.

**Chemical aspects.** Under typical operating conditions for atmospheric pressure-operated DFB gasifiers (i.e., 700°–900°C, steam-to-fuel [S/F] ratio >0.4) the conversion of the fuel is limited by kinetics rather than by thermodynamic equilibrium. In fact, the only relevant equilibrium in the gas phase is the water-gas shift (WGS) reaction, although the equilibrium is generally not fully attained [20]. The reaction rates ( $r$ ) are influenced by the composition of the fuel [21], operating conditions [22, 23], and the presence of catalysts [24]. Increasing the temperature, increasing the S/F ratio, and the selection of catalytic bed materials are commonly used strategies for increasing the rates of the reactions in gasifiers [25]. These aspects are discussed in Chapter 3.



**Figure 6.** Parameters that exert influences on fuel conversion by altering the fluid dynamics and the chemistry in the DFB gasifier. \*Parameters investigated in this thesis.

## 1.4 Aim and scope

The aim of this thesis was to identify strategies that would allow efficient control of the degree of conversion of solid biomass in fluidized bed reactors, in particular those parameters that influence the reforming of the biomass-derived hydrocarbons into valuable syngas. The ultimate goal of this thesis is a set of measures to control fuel conversion in DFB units, which will contribute to the rational design and reliable operation of DFB gasifiers, thereby creating and enabling a competitive alternative to traditional steam reforming of fossil feedstocks.

This thesis revisits the main findings in a series of six papers, which cover different aspects of biomass conversion in DFB gasifiers. Further details regarding the individual investigations can be found in the attached papers. Papers I and II uncover strategies to control fuel conversion that involve altering the fluid dynamics of the bed. Papers III–VI deal with the control of fuel conversion by influencing the chemistry within the gasification reactor. The impacts of temperature, S/F ratio, and the use of catalytic bed materials are investigated in the different papers. All the tested bed materials were applied in a DFB gasifier, except for feldspar in Paper

VI, in that the material was tested in a smaller downstream reformer with the ambition to using it in the gasifier at a later stage.

## 2 - Fluid-dynamics aspects of fuel conversion

---

### 2.1 Vertical mixing and volatiles-bed contacts

The mixing of fuel particles in the vertical direction is crucial when interactions between the fuel and bed material are desired, as is the case for an IG with in-bed catalyst. A lack of vertical mixing of the fuel particles and the bed material is known as segregation, and it arises when there are differences in the properties of the fluidized particles, mainly particle size and density, between the fuel and bed [26]. A lighter fuel is prone to move upwards (flotsam) with the rising bubbles created by the fluidizing gas, whereas the denser bed material particles tend to sink to the bottom (jetsam) of the reactor. The flotsam-like behavior of the fuel particles in a fluidized bed is accentuated for fuels that have a high content of volatiles, such as biomass and low-rank coal. This is due to the release of volatiles under hot conditions, with the subsequent formation of bubbles of volatiles, which tend to lift the fuel particles to the surface of the bed [27, 28].

The tendency of the lighter fuel to float has direct consequences for reactor design. For instance, it is commonly assumed that in-bed fuel feeding improves gas conversion because it prolongs the contact times between the volatiles and the bed material. This may be reasonable when the time-scales for devolatilization and vertical dispersion are similar [20]. However, when light and large devolatilizing biomass particles (e.g., commercial wood pellets) are used, the devolatilization time becomes longer than the rising time, which results in the release of volatiles mainly into the freeboard, regardless of the feeding position. In fact, limited differences in gas composition were quantified when comparing in-bed and over-bed feeding systems that used light fuels (wood, plastics) and a catalytic material in a 100-kW unit [17], and this was also the case in the 20-MW demonstration plant of GoBiGas [12]. In the present work, over-bed feeding was used in all the gasification tests, on the basis that the results should not differ significantly from those obtained in a similar reactor equipped with in-bed feeding.

Under cold conditions (i.e., without releasing the volatiles), the fuel segregation problems can be alleviated by improving the fluidization of the bed. Zhang et al. [18] have shown that some degree of vertical mixing can be induced by increasing the fluidization velocity. Maximal mixing was observed as the fluidization velocity increased, after which segregation took over again. A higher fluidization velocity also intensifies the ejection of particles into the freeboard [19], which presumably favors the contacts made between volatiles and bed material particles. For this reason, the fluidization velocity is a recurring parameter in the different investigations included in this thesis.

### 2.2 Horizontal mixing and residence time of the fuel particles

The residence time of the fuel particles in a DFB gasifier should be optimized rather than maximized. An insufficiently long residence time leads to incomplete devolatilization and/or incomplete conversion of the char, which results in a lower yield of product gas. Contrarily, if

the residence time is too long, the result is an unnecessarily high degree of char conversion, which limits the amount of fuel that is transported to the furnace. This needs to be compensated by, for example, the introduction of an auxiliary fuel or recirculation of the product gas to maintain the heat balance (see Section 1.2).

The residence time of the fuel depends on the motion of the fuel particles in the horizontal direction, which is typically characterized by a lateral dispersion coefficient ( $D$ ) [29]. The time-scale for lateral dispersion is given by Einstein's equation for Brownian motion [30]. At this point, it is important to emphasize that the approach commonly applied in the literature to estimate the residence time of the fuel particles in the bed is to assume plug flow of a well-mixed fuel [14]. As previously discussed, the fuel and the bed move differently, such that the fuel does not distribute evenly in the vertical direction [18]. Therefore, the assumption of a well-mixed fuel in the bed is dubious; the residence time of the fuel particles in a DFB reactor is more accurately described by the lateral dispersion coefficient.

The magnitudes of the dispersion coefficient reported in literature vary significantly, ranging from  $10^{-4}$  to  $10^{-1}$   $\text{m}^2/\text{s}$  [31]. This wide variation reflects the fact that fuel mixing depends on reactor size and operating conditions. Higher dispersion coefficients are usually obtained in fluid dynamically down-scaled reactors and under hot conditions [31, 32], which represent more accurately industrial applications. For a given reactor and fuel/bed material pairing, the lateral dispersion coefficient can be increased by increasing the fluidization velocity, as has been observed in a fluid-dynamically down-scaled reactor [33]. In the same investigation, the cross-flow was found to promote the transport of fuel particles from the inlet to the exit port of the reactor, although the impact of the cross-flow was less pronounced at low fluidization velocities.

## 2.1 Research approach

Understanding the mixing behavior of biomass allows one to decouple the impact of fluid dynamics on fuel conversion from the impacts of other operating parameters (e.g., S/F, temperature, catalysis). Therefore, the first part of this thesis (Papers I and II) was devoted to exploring the impacts of operating conditions on fuel mixing, thereby establishing the basis for interpretation of the results in the subsequent investigation. Two different experimental approaches were used.

Paper I aims to elucidate the extent of contacts between the bed material and the volatiles released from the fuel in a bubbling bed with over-bed feeding. The experimental method was based on a *tracer reaction* between the volatiles and the bed material particles. The reaction used was the fast oxidation of volatile species by an oxidized iron-containing material, ilmenite. As the product of the reaction is known, the composition of the product gas enables estimation of the fraction of the volatiles that has been in contact with the bed material particles ( $X_{\text{vol}}$ ). Further details of this approach can be found in Paper I.

Paper II revisits the impacts of fluidization velocity and circulation rate on fuel (horizontal and vertical) mixing, this time under high-temperature conditions in the Chalmers gasifiers. A digital image analysis (DIA) technique was used in this case. The surface of the fluidized bed was video-recorded with a camera probe, and the frames were analyzed subsequently. For vertical mixing, the tendency of the fuel to remain at the surface was quantified as the fraction of the batch of fuel particles that was detected at the surface of the bed. For horizontal mixing, the lateral dispersion coefficient and lateral velocity were determined. The outcome of this investigation is a set of qualitative trends that relate fuel mixing to the operational conditions (i.e., fluidization velocity, circulation rate of bed material).



## 3 - Chemical aspects of fuel conversion

---

### 3.1 Temperature and steam-to-fuel ratio (S/F)

The operational conditions in the gasifier, including the steam-to-fuel ratio (S/F) and temperature, affect the compositions of the produced permanent gas and tar species. An increase in the S/F ratio results in higher yields of  $H_2$  and  $CO_2$  due to enhancement of the WGS reaction [25]. The tar concentration typically decreases with increasing S/F ratio [34, 35], which is attributed to the promotion of steam reforming of hydrocarbons at higher partial pressures of steam. In a different investigation [22], it was found that steam promotes only the decomposition of the non-aromatic tar species, as the yield of aromatics was found to be unaffected by the level of steam under the conditions tested.

A higher temperature in the gasifier results in higher yield of permanent gases, enhancement of the WGS reaction, and lower tar concentrations [25]. The tar is affected not only in terms of the total amount formed, but also in composition. At a low temperature ( $<800^\circ C$ ), oxygenated compounds are present in significant quantities. Such species are closer in nature to the primary tar, which forms during the primary pyrolysis of the fuel [8]. According to the generally accepted scheme for tar maturation put forward by Elliot in 1988, a higher temperature (and longer residence time of the gas) favors the production of fewer but more aromatic compounds, such as benzene and naphthalene [36]. Such tar species are less reactive than the primary tar, and they are difficult to convert thermally at temperatures  $<900^\circ C$  [9].

In this work, the impacts of temperature and S/F ratio on fuel conversion were investigated using silica-sand as the bed material in the gasifier. Silica-sand is usually applied as a reference material in gasification research due to its low activity [15, 24], and it provides a reference for investigating operational conditions with limited interference from active species. Paper III investigates the impacts of the raw gas temperature and S/F ratio on the carbon balance. The impact of the S/F ratio is also investigated in the presence of active bed materials in Paper IV.

### 3.2 Catalytic bed materials

The catalysts used in commercial steam reformers are produced synthetically. Nickel is the most commonly used active metal, and refractory alumina or magnesium aluminate is used as the support material [37]. In IGs, natural ores are preferred over synthetic catalysts, as they offer a lower-cost alternative. For instance, olivine, which is a naturally occurring magnesium iron silicate, has been applied in several demonstration plants, including the Chalmers, Güssing [38], Milena [39], and GoBiGas [12] gasifiers. Natural catalysts are interesting substitutes for synthetic catalysts provided that they have sufficient activity towards steam reforming of hydrocarbons.

The activity of olivine has been partially attributed to its content of Fe, which turns into free reducible iron during heat treatment, e.g., through calcination [38]. Activation of other iron-containing materials, such as ilmenite, has been explained in terms of the migration of iron towards the surfaces of the particles, which is induced by successive redox cycles [40], thereby generating the amount of accessible iron needed for hydrocarbon reactions. Reduced forms of Fe have shown catalytic activities towards tar decomposition, and WGS reactions [41, 42]. This has encouraged researchers to use other iron-containing materials, such as Fe/olivine catalysts [43, 44] and ilmenite/sand mixtures [45], as in-bed catalysts for gasification systems. In Papers IV and VI, four bed materials in decreasing order of Fe content, i.e., ilmenite, olivine, bauxite, and feldspar, are investigated.

In the present study, all of the materials were used in-bed, with the exception of feldspar, which was used in a downstream reactor. Note that catalysts may alter the thermal maturation pathway of tar species, for example, by favoring alternative routes for the decomposition of the initial oxygenated tar compounds. Corella and co-workers have proposed that catalytic reforming of tar is more effective when applied in-bed than downstream, since the nascent tars in the gasifier are more reactive than the aromatic-rich tar that reaches the downstream reformers [46]. Therefore, the impact of feldspar on tar is anticipated to be different from the impacts of the other materials, simply because it is exposed to a more mature type of tar.

### **3.1 Impact of ash on catalyst activity**

Although ash species are minor components of biomass, they influence significantly the performances of the catalytic bed materials. The ash content of biomass ranges from 0.1% to several percentages w/w, depending on the fuel type, and the ash consists of inorganic species, such as Ca, K, Na, Mg, S, Si, P, Al, and Cl [47]. In combustion systems, the transformation of inorganic species has been investigated in relation to operational problems, such as corrosion, slagging, and bed agglomeration [48]. In gasification systems, the interest in ash species has also focused on their catalytic activities. For instance, alkali and alkali-earth metals (AAEM) are known to catalyze char gasification [49], the WGS equilibrium [50], and tar decomposition [24].

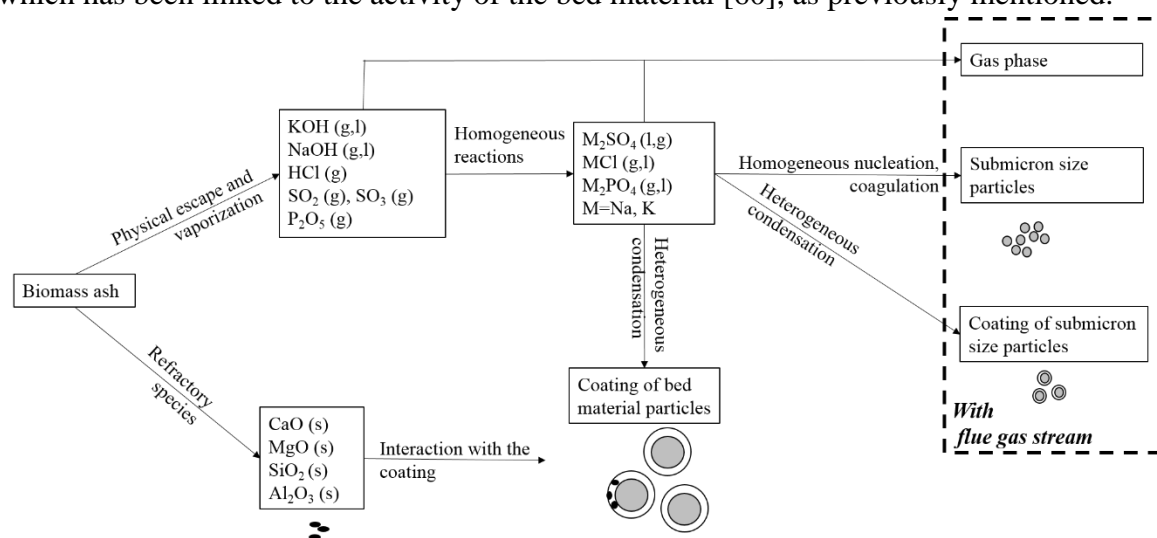
In recently conducted investigations [38, 51], the activity of the bed material has been partially ascribed to the ash coating that forms around the bed material particles. In contrast to the experience with traditional steam reformers, the inorganic impurities of the fuel benefit the activities of the catalysts used in steam gasification [50]. These inorganic species can be introduced with the fuel ash or/and they can be introduced deliberately as additives [52]. With olivine as the bed material, the use of additives rich in inorganics gives an effective decrease in the tar levels. For instance,  $K_2CO_3$  is used in the GoBiGas plant [12], and other non-revealed additives have been tested in the Milena gasifier [53]. In Paper IV, inorganic additives (K and S) are added to a bed of olivine to test for positive effects on fuel conversion.



The behaviors of inorganic species in alternating combustion/gasification environments, as happens in DFB systems, are not well understood [54]. Marinkovic et al. [51] have proposed that the catalytic activity of olivine is actually related to cycles of potassium uptake/release that are driven by the different gas atmospheres in the DFB. Based on thermodynamic considerations, it has been proposed that potassium is retained by the bed material as, for example,  $K_2SO_4$ , in the combustion side, and that it decomposes into catalytically active  $KOH$  (g)/ $KCO_3$  (g) in the reducing zones of the gasifier. A similar uptake/release cycle has been described for bauxite as the bed material [55], in which alkali species adsorb to the material in the furnace and desorb in the steam environment of the gasifier. This mechanism is equivalent to the adsorption/regeneration cycles investigated previously [56] for the removal of alkali vapors in combustors.

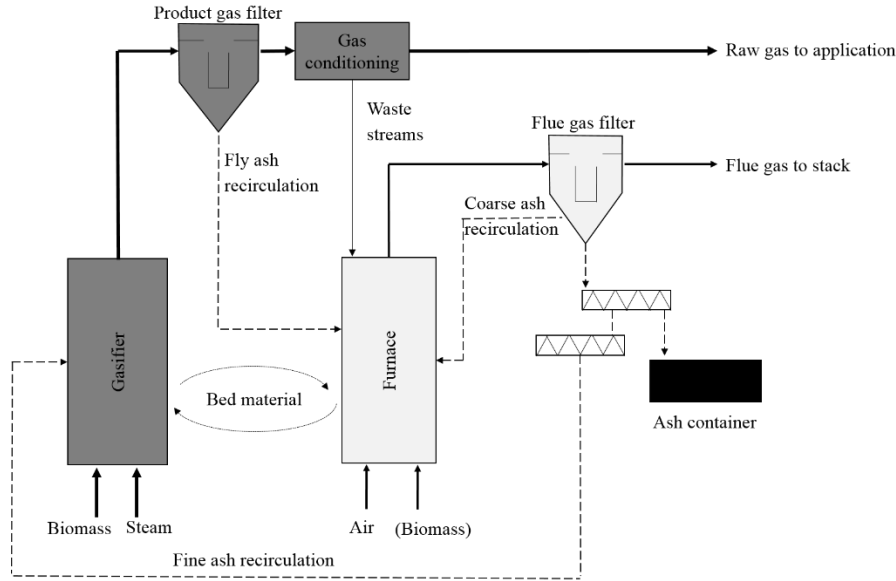
### 3.2 Flows of biomass ash in DFB gasifiers

At temperatures  $>700^\circ\text{C}$ , part of the inorganic content of the fuel, mainly comprising K, Na, Cl, S, and P, is released as vapors, whereas Al, Ca, Mg, and Si have a greater tendency to remain as solids [57, 58]. The subsequent evolution of the ash species under combustion conditions is summarized in Fig.7, based on previous descriptions [59] [57]. Eventually, the ash components exit the gasifier as: (1) gaseous species; (2) submicron-size particles formed by the nucleation of alkali vapors; and (3) condensate on the surfaces of existing particles. In fluidized beds, the interaction of alkali vapors with bed material particles initiates the ash-coating mechanism, which has been linked to the activity of the bed material [60], as previously mentioned.



**Figure 7.** Potential fates of ash-forming species following fluidized bed combustion of biomass fuels.

Taking as an example the existing DFB gasifiers (i.e., the 32-MW GoBiGas, the 8-MW gasifier at Güssing [54], and the 15-MW gasifier in Senden [61]) external loops of ash species are expected to exist in large DFB gasification plants. Figure 8 schematizes the flows of ash in a reference DFB gasifier. The small-size particles (i.e., fly ash), which are entrained by the flue gas and the raw gas, are subsequently removed by filters. As it contains significant amounts of unconverted carbon, the collected fly ash is recirculated to the combustor, so as to increase the efficiency of fuel conversion. The coarser ash, which is rich in bed material particles, may also be recirculated, with the goal of minimizing the loss of bed material to the system [54].



**Figure 8.** Ash flows in the DFB gasifier (as described in [54]).

In addition to the recovery of unconverted carbon, the recirculation of ash streams means that the inorganic species that originate from the fuel accumulate within the system. This can result in an increase in the thickness of the coating of the bed material particles. The bed material becomes a means to store and transport species between the reactors and to promote the previously mentioned uptake/release cycles. For instance, net transport of sulfur by the bed material from the furnace to the gasifier has been quantified in the DFB gasifier at Chalmers [62], and this can presumably also occur with other inorganic species. In fact, transport of potassium between reactors has been detected in the Güssing plant using ash balance calculations and bed material analyses [54].

### 3.3 Oxygen carriers

Oxygen carriers are materials that are capable of transporting oxygen from an oxidizing environment to a reducing environment. These materials have been investigated mainly in the context of Chemical Looping Combustion (CLC), in which the fuel is oxidized by the oxygen transported by the bed. Since it alternates between an oxidizing and a fuel-rich environment, the material experiences redox cycles, resulting in a net transport of oxygen from one vessel to the other.

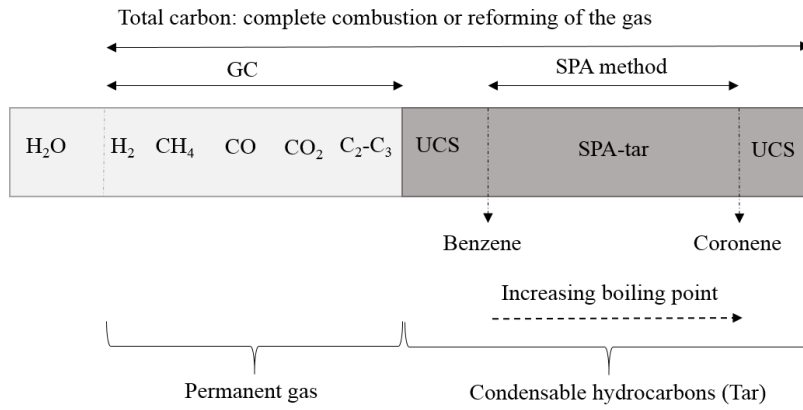
Oxygen-carrying capacity is a property associated with metallic species. Fe is an intensively investigated oxygen carrier that forms different oxides depending on the gas environment [63]. Other inorganic species, such as S, are also able to transport oxygen from the combustor to the gasifier, for instance by means of a sulfate/sulfide cycle in combination with Ca [64]. Although they are undesirable, oxygen carrier species are also present in DFB gasifiers, as they are part of the fuel ash and/or the bed material composition.

The observed impacts of oxygen transport on fuel conversion are: 1) oxidation of a fraction of the gases derived from the fuel; and 2) increased char conversion, as compared with equivalent tests with inert silica-sand as the bed material [65]. The higher rate of char conversion in the presence of oxygen carriers is attributed to the lower concentrations of inhibiting species, mainly  $H_2$  and tar species, surrounding the char particles [66, 67]. The impacts of oxygen transport on tar species are described in Paper III, while the impacts on char conversion are investigated further in Paper V.

### **3.4 Research approach**

The impacts of operating conditions (Paper III) and catalytic materials (Papers IV and V) on fuel conversion were investigated experimentally in the DFB gasifier at the Chalmers University of Technology, with the aim of reproducing conditions relevant to industrial applications, e.g., long-term exposure of the bed material to biomass ash. A small downstream reformer was applied in Paper VI, as this was a preliminary investigation of feldspar prior to subsequent use in the gasifier. The main tool applied in this part of the thesis is the mass balance over the gasifier reactor, and the conversion indicators used for comparing the experimental cases are as follows: (1) yields of permanent gases species; (2) yields of tar; and (3) total carbon conversion. For proper closure of the mass balance, a thorough quantification of the species was required.

Quantification of the complete spectrum of raw gas species is difficult due to the wide range of species involved. The permanent gases consist of  $H_2$ , CO,  $CO_2$ , and hydrocarbons that range from  $CH_4$  to  $C_3H_8$ , which are readily detectable by gas chromatography (GC). The condensable hydrocarbons can be determined using the Solid Phase Adsorption (SPA) method [68], which allows for quantification of species with boiling points between those of benzene and coronene [69]. However, this may not be sufficient to cover the entire spectrum of the condensable hydrocarbons. As described in Fig.9, condensable species may be present that are out of the SPA-measurable range, herein referred to as ‘unknown condensable species’ (UCS). To close the carbon balance, the carbon content of the UCS can be determined indirectly based on the difference between the total carbon in the raw gas and the carbon in the measured species (i.e., by SPA and GC) [70]. The total carbon in the raw gas can be determined by either fully combusting [71] or fully steam reforming [70] the gas stream, followed by GC measurements of the resulting CO and  $CO_2$ .



**Figure 9.** Raw gas spectrum and measurement methods.

Identification of all the species in the raw gas is not essential for monitoring industrial units. Larsson et al [7] have described how the performance of a gasifier can be estimated by means of the H/C and O/C molar ratios of the permanent gases, considering only the species CO, CO<sub>2</sub>, and H<sub>2</sub>. Nevertheless, elucidation of fuel conversion requires a comprehensive understanding of the carbon balance throughout the reactor. Failure to quantify all the carbon streams hinders the quantification of the degrees of conversion of char and condensable species. For this reason, the emphasis in this work is on closing the carbon balance of the conducted experiments, thereby enabling assessments of char and tar conversion to complement the permanent gas measurement.

## 4 - Experimental

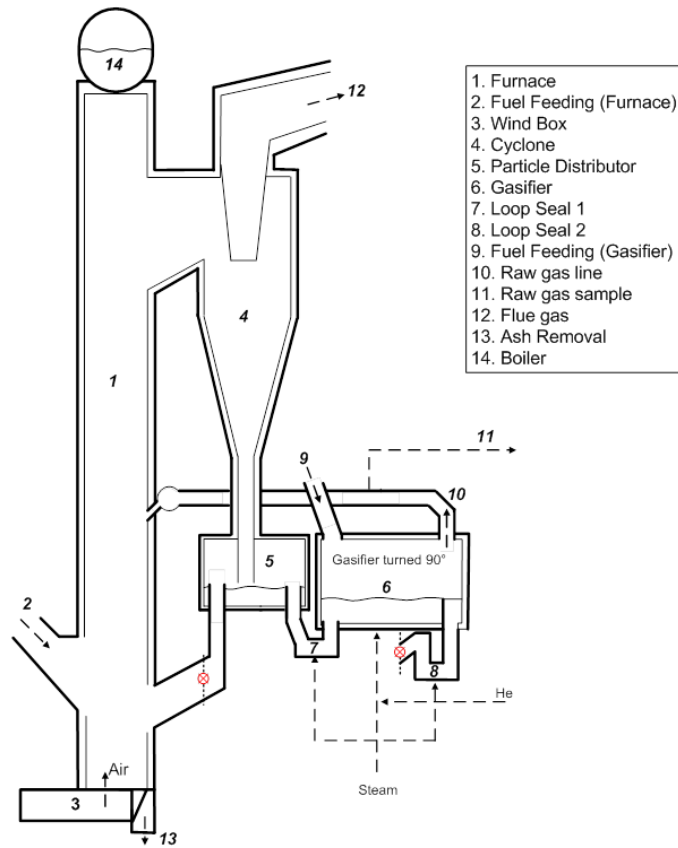
---

### 4.1 Gasifier

The DFB unit at Chalmers consists of a 2–4-MWth gasifier that is coupled to a 12-MWth boiler. A simplified schematic of the system is given in Fig.10. The gasifier has a cross-sectional area of  $1.44 \text{ m}^2$ , and it operates in a bubbling regime, while the boiler is a circulating fluidized bed (CFB) with cross-sectional area of  $2.1 \text{ m}^2$  and height of 12 m. The boiler is operated continuously during the winter season, as it provides heat to the Chalmers campus. In this case, the bed material by-passes the gasifier, flowing directly from the particle distributor (5) back to the combustor (1). During the gasification experimental campaigns, the circulation of bed material between the reactors is enabled by fluidizing the inlet and exit Loop Seals (7-8), the gasifier (6), and the particle distributor (5). The return of the bed material from the gasifier to the boiler is represented by a red circle in the figure.

The gasifier is fluidized with steam and the fuel is fed by gravity (9) onto the surface of the bubbling bed. For safety reasons, fuel feeding to the gasifier is carried out only between 6 am and 6 pm approximately, which corresponds to the operator's shift. A small stream of dry flue gases from the boiler is used as the purge gas in the fuel-feeding system, to prevent air from entering the gasifier. Commercial wood pellets are used as the fuel in the gasifier, and typical operating conditions are  $810^{\circ}\text{--}820^{\circ}\text{C}$  and a sub-atmospheric pressure of 1–2 kPa. Simultaneously, the boiler is fed with wood chips (or a wood chips/pellets mixture) to ensure that sufficient heat is supplied to the campus and to enable flexible operation of the gasifier, e.g., adjustment of bed temperature at the inlet of the gasifier.

A peculiarity of the Chalmers system is that the raw gas produced in the gasifier returns to the combustor (arrow 10 in Fig.10), where it is combusted. This setup is suitable for research purposes, whereas in a commercial unit the raw gas would go through the gas cleaning steps and thereafter enter the final application or undergo further processing. An advantage of this configuration is that the fly ash from the gasifier and other gaseous inorganic species are returned to the combustor, mimicking the fly ash flows in large units (see Section 3.2). In fact, the recirculation of inorganic species in the Chalmers setup conveniently imitates the flows of inorganics in the existing 32-MW DFB gasifier in the GoBiGas demonstration plant.



**Figure 10.** Schematic of the Chalmers DFB gasifier.

#### 4.1.1 Camera probe

The camera (Unibrain model 630b) used for direct observation of the hot gasifier bed was placed inside a probe, and it was accommodated inside a gas-tight port at the wall of the gasifier. The probe was equipped with a cooling jacket that contained water as the cooling medium. The temperature of the compartment was maintained at 25°C to avoid cracking the front glass through thermal stress. During the tests, the tip of the probe was purged with nitrogen, to avoid condensation of tars and to remove any sand particles. A lens capable of withstanding temperatures up to 1000°C was placed between the front glass and the camera.

The experiments reported in Paper II were conducted with controlled batches of fuel, which were fed into the gasifier once the operational conditions (i.e., temperature, fluidization, rate of circulation of the bed material) were stable. Each experimental case was recorded for approximately 3 minutes, to cover from the time period from batch feeding to the last fuel particle exiting the reactor. The batches were relatively small (~200 pellets), so to allow discrimination of the individual particles in the frames.

#### 4.1.2 Gas analysis

All the raw gas measurements were conducted in two separate slipstreams (~10 Ln/min), which were sampled at the raw gas channel (11) and after the hot filter. The filter and the sampling

lines were heated to 350°C, to prevent the condensation of hydrocarbons. A small flow of helium (~20–30 Ln/min) was used as a tracer gas for the quantification of the total dry gas flow per unit of fuel. Helium was added to the fluidization steam, as indicated in Fig.10, thereby enabling quantification of the yields of the raw gas species (in units of mol/kg daf fuel). Slipstream 1 was used for sampling the tar and permanent gas, whereas Slipstream 2 was led into a High-Temperature Reactor (HTR) for quantification of the total carbon in the raw gas.

Tar samples were acquired according to the solid-phase adsorption (SPA) method [68]. At least three samples were obtained for each experimental case, and the results presented are the average values of these samples for each case. The tar sampling during the campaign with bauxite was conducted with LC-NH<sub>2</sub> columns, which showed limited adsorption of BTX species. The sampling method was improved for the subsequent campaigns by using instead the Supelclean ENVI – Carb/NH<sub>2</sub> SPE columns, and this resulted in 7–10-fold higher adsorption of the BTX species compared to the LC-NH<sub>2</sub> columns. The accuracy of the improved method was validated by using the HTR. The SPA samples were eluted with a solvent, and the solution was analyzed in a GC equipped with a flame ionization detector (GC-FID), as described previously [69]. The GC-FID system used comprised the BRUKER GC-450 and GC-430, and species in the range from benzene to coronene were detected.

Downstream of the SPA sampling port, the raw gas was cooled, filtered, and analyzed in a micro-gas chromatograph ( $\mu$ -GC), to quantify the permanent gas components. The  $\mu$ -GC used was the Varian CP4900, equipped with Poraplot Q and MS5A columns and using He and Ar as carrier gases, respectively. The species assayed were H<sub>2</sub>, He, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>x</sub>, and N<sub>2</sub>. Further details of the gas-conditioning system can be found elsewhere [24].

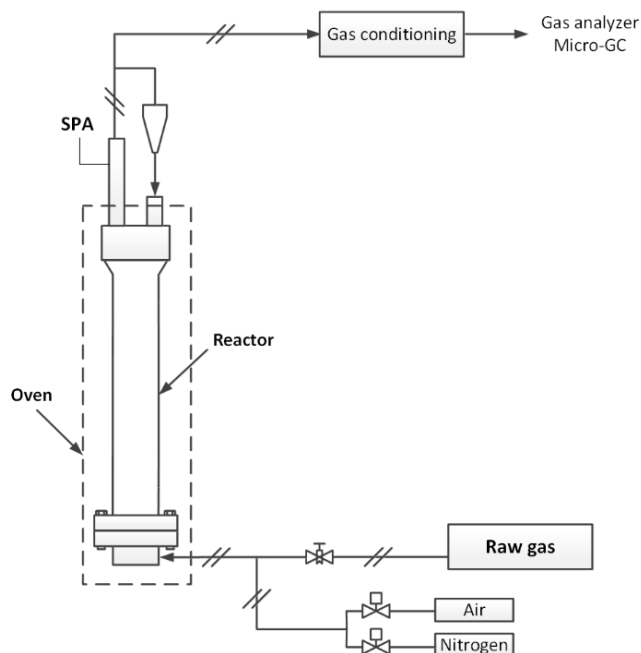
The quantification of total carbon was accomplished by means of a HTR. In brief, the HTR consisted of a ceramic tube reactor inserted into an electrically heated oven. The oven was maintained at 1700°C, and the raw gas from the gasifier was led towards the reactor *via* a line that was electrically heated to 350°C. The raw gas flowed through the ceramic tube, where all the hydrocarbons were decomposed into CO<sub>2</sub>, CO, and H<sub>2</sub>. The stream at the exit of the ceramic reactor was filtered and cooled to remove the water content; and the dry gas was thereafter analyzed in the  $\mu$ -GC. The  $\mu$ -GC used was the Varian CP4900, equipped with MS5A and Poraplot U columns and using Ar and He as carrier gases, respectively. By calculating a mass balance throughout the HTR, the elemental flows of CHO that exited the gasifier as dry hot gas were determined. The detailed mass balance calculations and complete physical configuration of the HTR have been described by Israelsson et al [70].

## **4.2 Downstream fluidized bed reformer**

The reactor system used in Paper VI consisted of a tube with an inner diameter of 55 mm and a length of 379 mm, which contained a porous plate that served as the gas distributor. The reactor contained a bed of 200 g of unused feldspar material, which had the properties listed in Table 4 and Table 5. The material was fluidized with either a mixture of air/nitrogen or raw gas generated in the Chalmers gasifier. The gasifier was operated with inert silica-sand to ensure a

high tar load in the inlet gas. As shown in Fig.11, the reformer reactor was inserted in an oven, which could reach up to 900°C. The performance of the catalyst was assessed at three different temperatures: 700°C, 800°C, and 900°C.

Gas and tar measurements of the inlet and outlet gas were taken according to the descriptions above (Section 4.1.2). Note that the HTR was not used in these tests, as the sampling line that is usually led to the HTR reactor was, in this case, led to the downstream reformer. Therefore, quantification of the total condensable species was not possible, and the only tar measurements available are those derived from the SPA samples.



**Figure 11.** Downstream reformer.

### 4.3 Bed materials tested

The bed materials tested in this thesis were: silica-sand; ilmenite; bauxite; olivine; and feldspar. The fluidization properties of all the materials are listed in Table 4, and their chemical compositions are summarized in Table 5.

**Table 4.** Physical and fluidization properties of the materials tested.

	Silica-sand (gasifier)	Olivine (gasifier)	Bauxite (gasifier)	Ilmenite (gasifier)	Feldspar (downstream of the gasifier)
Particle density (kg/m <sup>3</sup> )	2650	3300	3000	4200	2600
$d_p$ (μm)	316	288	305	195	125–180
Minimum fluidization velocity <sup>a</sup> , $u_{mf}$ (m/s)	0.04	0.05	0.05	0.03	0.01
Terminal velocity <sup>a</sup> , $u_t$ (m/s)	2.7	2.8	2.8	1.8	1.0
Range of fluidization number tested <sup>a</sup> , $u_o/u_{mf}$	3–4	2–6	3–4	5–10	

<sup>a</sup> Steam at the average bed temperature.



**Table 5.** Chemical composition (% w/w) of the materials tested in this thesis.

	<b>Silica-sand (gasifier)</b>	<b>Olivine (gasifier)</b>	<b>Bauxite (gasifier)</b>	<b>Ilmenite (gasifier)</b>	<b>Feldspar (downstream of the gasifier)</b>
<b>SiO<sub>2</sub></b>	99.2	41.7	6.50	0.40	67.5
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.17	0.46	88.50	0.35	18.8
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.054	7.4	1.10	35.0	0.11
<b>Ti<sub>2</sub>O</b>			3.0	51.0	0.01
<b>MgO</b>		49.6		1.00	0.04
<b>Cr<sub>2</sub>O<sub>3</sub></b>		0.31		0.30	
<b>NiO</b>		0.32			
<b>MnO<sub>2</sub></b>				1.30	<0.0078
<b>V<sub>2</sub>O<sub>5</sub></b>				0.23	
<b>Na<sub>2</sub>O</b>					4.3
<b>K<sub>2</sub>O</b>					8.4
<b>CaO</b>					1.2



## 5 - Results and discussion

### 5.1 Vertical and horizontal mixing of the fuel

The fuel mixing behavior in the gasifier was investigated by direct observation of the bed surface with a video camera. Table 6 summarizes the general trends identified for fuel mixing in both the vertical and horizontal directions when the fluidization velocity and circulation rate of the bed material were varied. The fuel particles tended to move faster from the inlet of the gasifier to the exit with increasing fluidization velocity, as well as with increasing circulation of the bed material. The relationships between lateral dispersion and cross-flow became clearer at higher fluidization velocities, most likely because the fuel was well-mixed in the vertical direction and it followed more easily the bulk of solids. These trends support the findings of previous investigations [33], and they indicate that the residence time of the fuel can be controlled by modulating these two operating parameters. Furthermore, the lateral dispersion coefficient was in the range of  $10^{-1}$ – $10^{-2}$  m/s, which is in the same order of the values obtained in previous studies conducted under hot conditions [31] and with fluid-dynamically downscaled reactors [32].

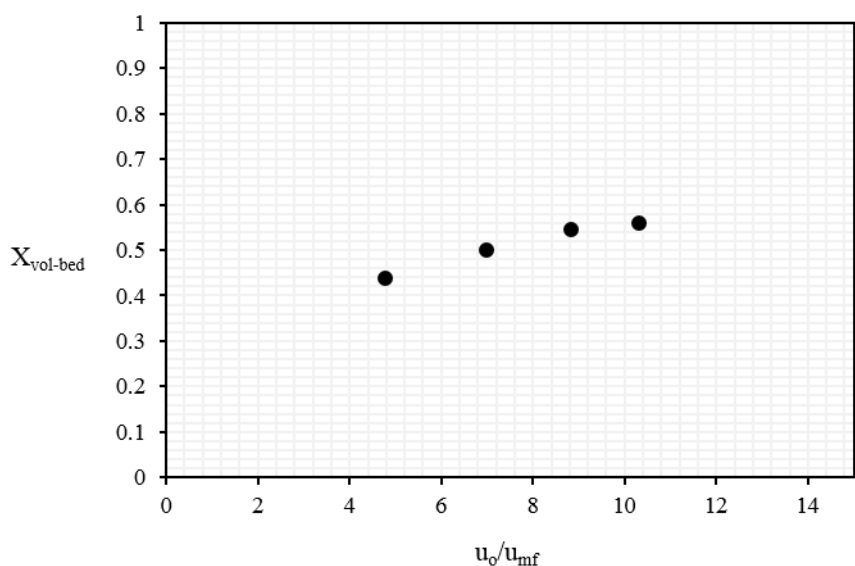
**Table 6.** Qualitative trends for fuel mixing with changes in fluidization velocity and circulation rate of the bed material. Increase: ↗. Decrease: ↘.

Operating parameter	Change	Impact on horizontal mixing	Impact on vertical mixing
Fluidization velocity	↗	↗	↗
Circulation rate of the bed material	↗	↗	↘

The tendency of the fuel particles to remain on the surface of the bed was also affected by the fluidization velocity and the rate of solids circulation. The trend was clear at all circulation rates tested: a higher fluidization velocity resulted in a smaller fraction of the fuel particles being detected on the surface of the bed. This indicates that despite the tendency of the light fuel to float, some degree of mixing can be induced by modifying the fluidization velocity, which is in line with the observations made by Zhang et al [18] for experiments conducted under cold conditions. It was also found in the present study that vertical mixing could increase until it leveled off, and that further mixing could not be achieved by altering the fluidization velocity. In contrast to the findings of Zhang et al, we did not observe a negative effect of fluidization velocity on vertical mixing under the conditions tested. The observations based on the video recordings were consistent with the estimated extent of contacts between the volatiles and bed material shown in Fig.12, where higher fluidization velocity increased the fraction of volatiles in contact with the bed.

An important outcome from Paper I was showing that there is a significant extent of contacts between volatiles and bed material under the conditions tested. A conservative estimate of the fraction of volatiles in contact with the bed ( $X_{vol}$ ) is 44%, which corresponds to the lowest

fluidization velocity tested. The estimated extent of contacts is surprisingly high given the simple reactor design used in this work and the tendency of the biomass particles to segregate. First, the fuel was fed by gravity from the top of the reactor, which is commonly regarded as the fuel-feeding option that generates the poorest gas-solid contacts, as compared with in-bed feeding [17]. Second, the reactor has a simple rectangular cross-sectional architecture without any internal elements to enhance fuel mixing or to induce turbulence [16]. The results indicate that a reasonable degree of gas-solid contacts can be attained with the mixing generated by the freely bubbling bed, provided that the bed is well-fluidized. In the present investigation, and at cross-flow values typically used in the Chalmers unit, the bed could be considered to be well-fluidized at fluidization numbers  $(u_o/u_{mf}) > 5-6$ , as observed in the video recordings taken of the surface of the bed.



**Figure 12.** Estimated fraction of volatiles ( $X_{vol-bed}$ ) in contact with the bed material as a function of fluidization number ( $u_o/u_{mf}$ ).  $X_{vol-bed}=1$  indicates that all the volatiles have been in contact with the bed.

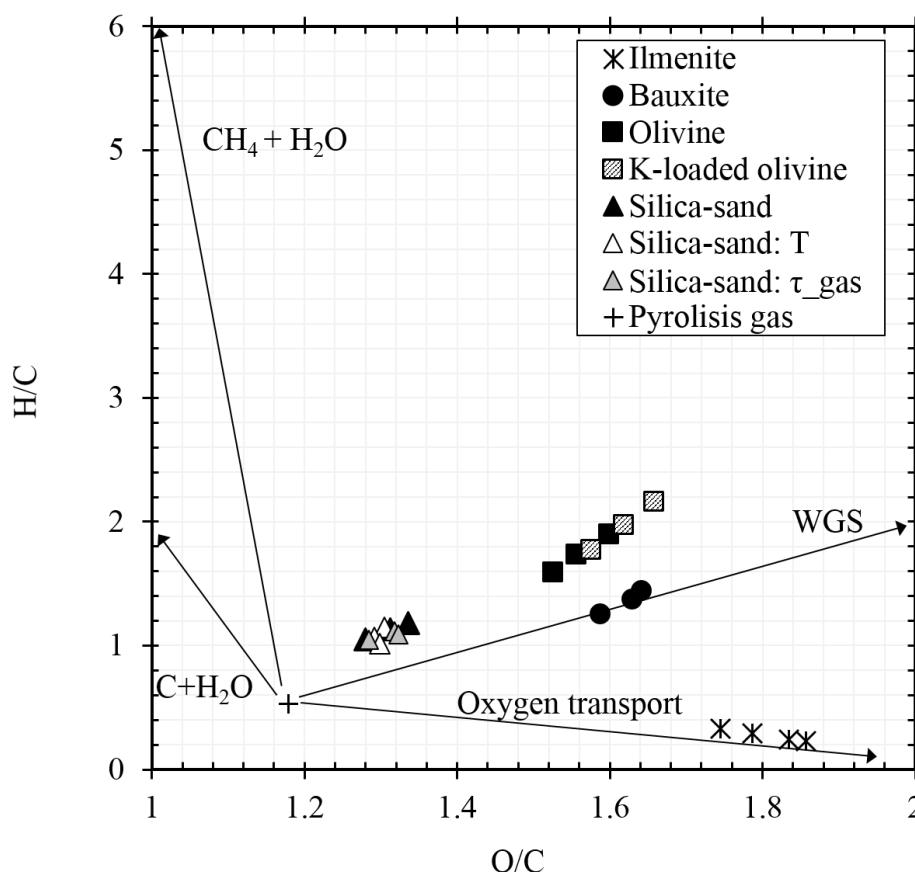
## 5.2 Operating conditions and active materials

**Permanent gas.** Figure 13 shows the permanent gas composition as the molar ratios of H/C and O/C for the different bed materials tested under similar operational conditions [7]. The series for silica-sand included all the cases with different S/F ratios (S/F range: 0.75–0.98), average temperatures of the raw gas ( $T_{gas}$  range: 744°–774°C), and residence times of the raw gas ( $\tau_{gas}$  range: 3.95–5.49 s). Unless otherwise indicated, the cases that belong to the same series correspond to increasing S/F ratio, as one moves from left to right in the figure. The S/F ratio was here changed by increasing the fluidization steam at a constant rate of fuel feeding, which implies that gas-solid mixing is improved by an increase in S/F ratio.

For similar operational conditions, the permanent gas composition was dependent upon the type of bed material. In fact, the bed material type had a stronger impact on the permanent gas composition than any change in the S/F ratio or the temperature in an inert bed, which indicates that the non-catalyzed homogeneous reactions are slow, e.g., the WGS reaction and steam

reforming of hydrocarbons. By changing the bed material, a drastic change in the composition of the raw gas could be achieved. When comparing the cases using catalytic and inert bed materials, the main differences in the composition of the permanent gas corresponded to the extent of the WGS reaction, while oxygen transport exerted the strongest impact on the permanent gas composition when ilmenite was used as the bed material. In Fig.13, the cases with bauxite as the bed material fall between those corresponding to ilmenite and olivine, as bauxite exhibits catalytic properties and oxygen transport capacity.

For all the bed materials tested, an increase in the S/F ratio led to a more prominent WGS reaction, which proceeds with a slope of 2 in Fig.13. For the oxygen carrier ilmenite, the increase in S/F ratio resulted in higher transport of oxygen, which was manifested as an increase in the O/C ratio, while the H/C ratio decreased. The marginal change in composition induced by a change in S/F ratio was larger for active materials than for a similar case with a bed of silica-sand. This can be explained by the better contact between the active bed material and the volatiles released from the fuel.

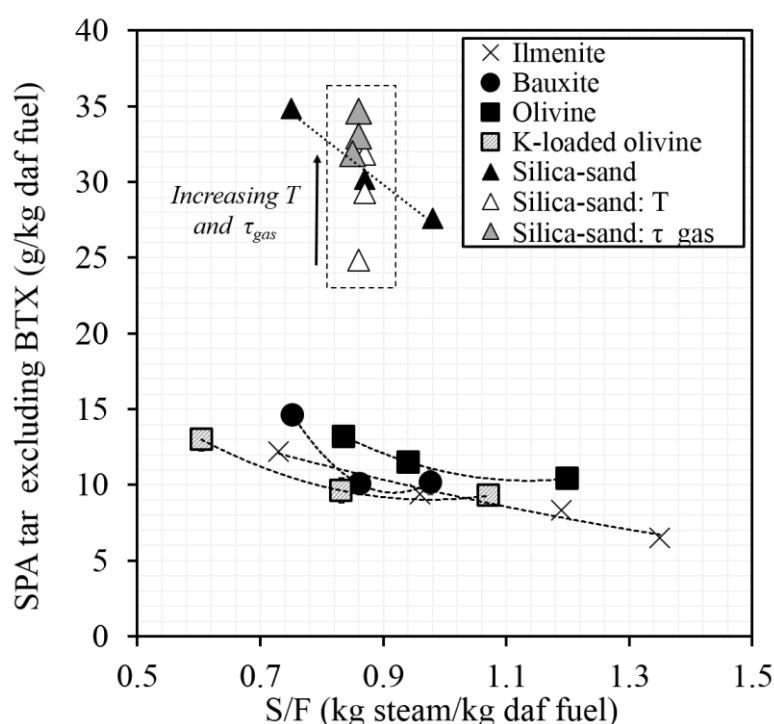


**Figure 13.** Molar H/C and O/C ratios of the syngas species (i.e., H<sub>2</sub>, CO, and CO<sub>2</sub>) corresponding to the operation of the Chalmers gasifier with different bed materials. For each series, the S/F ratio increases from left to right. The pyrolysis gas is from a pyrolysis experiment conducted in an N<sub>2</sub> atmosphere [7]. Silica-sand was used for a wide range of operating conditions (S/F, T, and τ<sub>gas</sub>).

**Condensable hydrocarbons (tar).** The tests conducted with inert silica-sand as the bed material revealed the thermal decomposition pattern of tar under the conditions tested. In

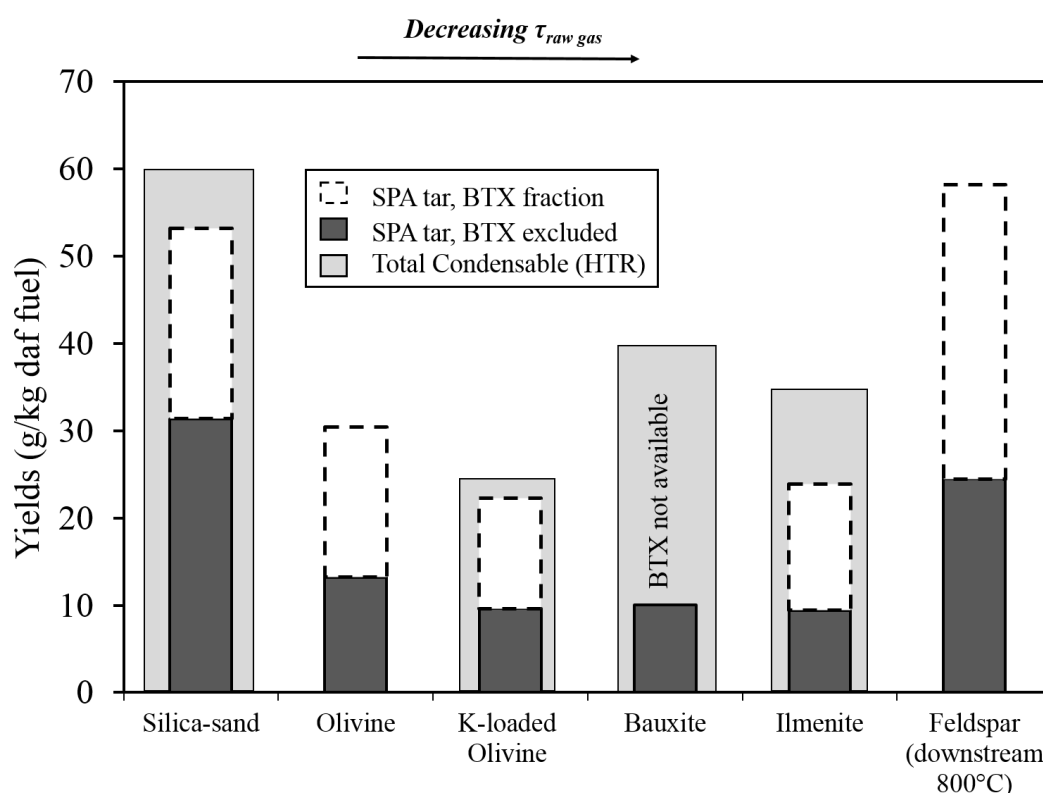
Fig.14, the application of more-severe operational conditions, in terms of residence time ( $\tau_{\text{gas}}$ ) and/or temperature (T), resulted in a higher conversion rate of primary tar to more aromatic species. The apparent increase in SPA-measurable tar should not be interpreted as an increase in the total yield of condensable species, but instead as an increase in the measurable part only, i.e., the aromatic compounds. The same reasoning is applicable to the apparent decrease in tar level with higher S/F ratio, which is actually the result of a lower degree of maturation of the total tar as the residence time is shortened by the higher flow of gases. The measurements indicate that the fraction of condensable species that cannot be detected by the SPA method (i.e., the UCS) is most likely primary tar species, as these species evolve according to the tar maturation scheme [36].

With active bed materials, the SPA method gave a good indication of the yield of total condensable species. For instance, increasing the S/F ratio (Fig.14) resulted in a decrease in the amount of SPA-measurable tar for the active bed materials, and the yield of total condensable species was also lower. In fact, in most cases, the SPA-measurable tar together with the permanent gas was sufficient to close the carbon balance, indicating a negligible amount of UCS. This outcome was possible owing to the use of improved SPA sampling tubes, which adsorb efficiently the BTX fraction, as mentioned in the *Experimental* section.



**Figure 14.** Levels of SPA-measurable tar (excluding BTX) as a function of the steam-to-fuel ratio. Each series corresponds to a different bed material in the Chalmers gasifier under similar operating conditions. Silica-sand was used under a wide range of operating conditions (S/F, T, and  $\tau_{\text{gas}}$ ). For the silica-sand series, the temperature and residence time of the gas increase from the bottom to the top of the graph.

Under the conditions tested, the non-catalyzed aromatization of primary tar species appeared to play a significant role in altering the tar composition, as observed in the cases with silica-sand as bed material. However, the non-catalyzed steam reforming of hydrocarbons into  $H_2$  and  $CO$  seemed to be limited, as the permanent gas remained essentially the same across the different cases (see silica-sand cases in Fig.13). In contrast, when active bed materials were applied, the level of SPA-measurable tar was approximately 3.5-times lower than that obtained during the runs with inert silica-sand as the bed material (see Fig.14). This large difference is due to the conversion of condensable species into permanent gas through the catalytic action of the bed material, as confirmed by the HTR measurement (Fig.15).



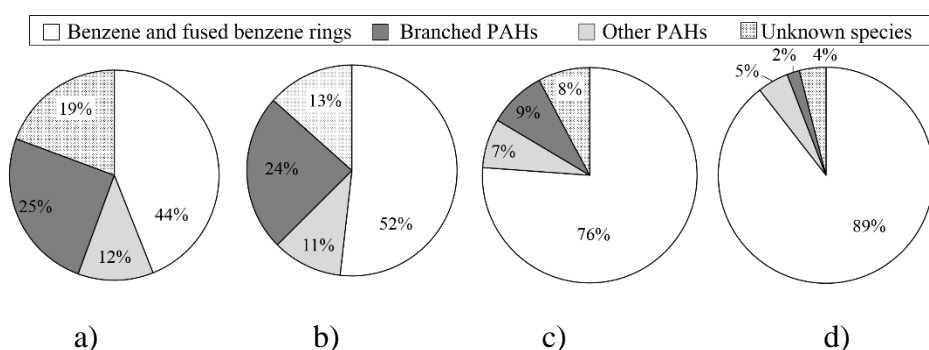
**Figure 15.** Levels of SPA-measurable tar and total condensable species (in g/kg daf fuel) obtained with different bed materials in the Chalmers gasifier. Steam-to-fuel ratio 0.8 and bed temperature approximately 820°C.

The lowest yield of total condensable species was achieved by the addition of potassium into a bed of olivine (termed the *K-loaded olivine* case).  $K_2CO_3$  was added together with elemental sulfur on the first day of operation, when the olivine showed limited signs of activity. On the second day of operation, the activity of the K-loaded olivine towards tar species was higher than that of a bed of olivine that had been operated in the Chalmers system for approximately 1 week (the *Olivine* case). Both the conversion of tar species and the WGS reaction were catalyzed to a greater extent by K-loaded olivine, mirroring the experience at the GoBiGas plant [12].

For comparison purposes, the case with feldspar is included in Fig.15, although feldspar was tested in a downstream reformer, whereas the other bed materials were applied inside the

gasifier. The inlet gas to the reformer had presumably a higher tar content than the silica-sand case presented in Fig.15, as the temperature of the gasifier was somewhat lower during the reformer tests. However, as previously mentioned, the HTR could not be used during this test, and only the SPA-measurable tar was quantified. Nonetheless, the levels of condensable species in the raw gas (Fig.15) clearly indicated that the reduction in SPA-measurable tar in the downstream reformer was far less prominent than that obtained by applying a catalytic material inside the gasifier. In fact, the most noteworthy change in the gas during the feldspar test was the speciation of the tar.

In the downstream reformer, a larger proportion of benzene and fused benzene rings (i.e., naphthalene, phenanthrene, anthracene, pyrene, and chrysene) were produced; benzene and naphthalene were by far the most dominant species. The increases in the levels of these pure aromatic rings were amplified at higher temperatures, while the branched polycyclic aromatic hydrocarbons (PAHs), and other PAHs were reduced, as shown in Fig.16. The efficiency of the conversion of tar in a downstream reactor may differ depending on the nature of the bed material applied, as each catalyst exhibits selectivity for different species. Nevertheless, the results indicate that a downstream reformer could be suitable for narrowing the spectrum of tar species in the raw gas, from a wide variety to a limited number of species. In this case, benzene and fused-benzene rings were mainly formed.

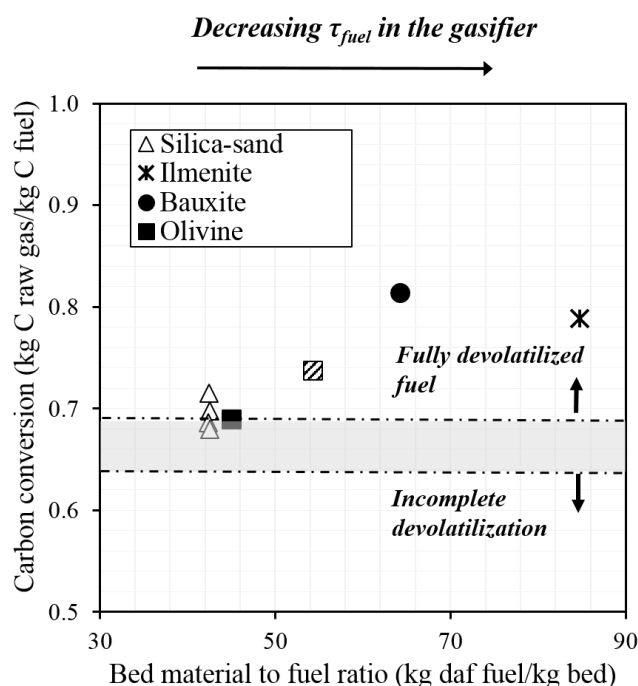


**Figure 16.** Shares (% w/w) of tar species: a) in the raw gas at the inlet of the reformer; and at the exit of the reformer operating at b) 700°C, c) 800°C, and d) 900°C. The bed material in the reformer was feldspar. Benzene and fused benzene rings: benzene, naphthalene, phenanthrene, anthracene, pyrene, and chrysene. Branched PAHs: toluene, xylenes, (methyl)-styrene, methyl-naphthalene, phenolic compounds. Other PAHs: heterocyclic species, PAHs containing other rings than benzene. Unknown species: species that were detected by GC-FID but not identified.

**Total carbon conversion.** The degree of carbon conversion ranged from 67% to 82% depending on the bed material used in the gasifier, and it was generally higher for those cases in which active bed materials were used, as compared to the reference case with silica-sand as the bed material. The higher percentage carbon conversion obtained with active bed materials could not be correlated to changes in residence time of the fuel particles in the gasifier. Therefore, the higher level of char conversion can be attributed to an increase in the kinetics of the steam gasification reaction, which indicates catalytic gasification and/or reduced inhibition of the gasification reaction.

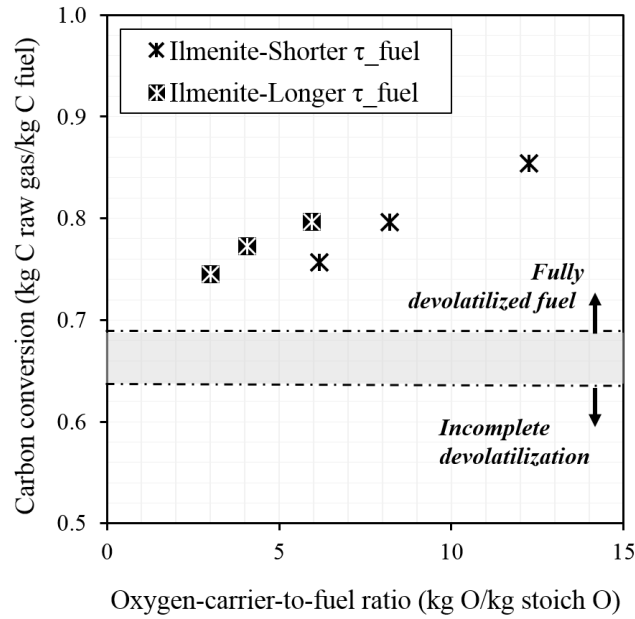


In the case of the oxygen carrier ilmenite, the enhanced kinetics could be the result of lower inhibition by volatile species, as proposed in the literature [65, 72]. However, for the catalytic materials olivine and bauxite, the oxygen transport effect is modest compared to that of ilmenite (Fig.13), and oxygen transport cannot explain the high char conversion on its own. With respect to the catalytic materials, char gasification can be enhanced by active species released by the bed material, which are subsequently adsorbed into the char matrix, as proposed by others [49]. The results indicate that the release of catalytic species from the bed material into the gas phase is a significant phenomenon under conditions relevant to DFB gasification.



**Figure 17.** Total carbon conversion as a function of the rate of circulation for different bed materials tested in the Chalmers gasifier. All the presented tests were carried out at a similar steam-to-fuel ratio ( $S/F \sim 0.8$ ).  $X_c=1$  for full conversion of the fuel into product gas. The silica-sand case includes cases at different temperatures ( $T_{bed} = 786^{\circ}\text{--}823^{\circ}\text{C}$ ). The shaded area represents the carbon conversion required for full devolatilization of the fuel.

It can be inferred that the char conversion is controlled by the availability of the active species carried by the bed material, which can be expressed as the ratio of the flows between the active species and the fuel. This hypothesis was tested in Paper V using the oxygen carrier ilmenite, and the results are summarized in Fig.18. The circulation rate of the bed material is expressed as the stoichiometric ratio of oxygen, i.e., the oxygen-carrier-to-fuel ratio ( $\phi$ ) [73], as the major active species is most likely the oxygen carried by the bed. Additional releasable alkali may be transported by the bed [49], as previously discussed. Nevertheless, there is a consistent response of char conversion to changes in  $\phi$ , which confirms the hypothesis. The shorter residence time of the fuel was overcompensated by the increased availability of the active species per unit of fuel.



**Figure 18.** Total carbon conversion in a bed of oxygen-carrier material (i.e., 100% ilmenite) as a function of the oxygen-carrier-to-fuel ratio. A shorter residence time of the fuel ( $\tau_{fuel}$ ) is achieved with a higher rate of circulation of the bed material. Stoichiometric conditions correspond to an oxygen-carrier-to-fuel ratio of 1. The shaded area represents the carbon conversion required for full devolatilization of the fuel.

### 5.3 General discussion

Changing the operational conditions (e.g., temperature and steam-to-biomass ratio) in a bed of chemically inert silica-sand resulted in a marginal improvement in fuel conversion, as compared to the benefits of applying catalytic bed materials. This reveals that under typical DFB gasification conditions, the conversion of the fuel is limited by the relatively slow kinetics of hydrocarbon and char conversion. In fact, even the gas-solid contacts seem to be satisfactory with the higher range of fluidization velocities tested. Note that in Fig.14, for instance, higher fluidization (i.e., higher S/F ratio) does not result in a dramatic reduction of tar yield. Only at very low fluidization velocities does the lack of fuel mixing become an important limitation for the reactions, which may explain the somewhat higher yield of tar on the left-hand side of Fig.14. Provided that there is a sufficient level of fluidization, a reasonable degree of gas-solid contacts can be attained.

In line with the slow kinetics of hydrocarbon conversion, the use of in-bed catalysts becomes crucial to achieving steam reforming of tar species in the gasification reactor. Natural minerals, such as olivine, have been shown to have high-level activities towards tar decomposition in the Chalmers DFB, as well as in other pilot and demonstration plants [12, 38, 39]. The traditional challenges faced by commercial steam reforming catalysts, such as catalyst deactivation by carbon deposition and sulfur poisoning, seem not to be relevant to DFB gasifiers that employ natural bed materials. It was anticipated that the carbon deposits would not cause deactivation

of the catalyst in the DFB system, since they would be burnt in the combustor side. The impacts of inorganic impurities, in particular sulfur, were more surprising, as they were found to enhance the activity of the catalyst rather than cause any noticeable poisoning. A strong potential exists for further optimization of the catalytic activities of natural materials, for instance through the use of additives. The present results show that the activity of olivine can be controlled by adjusting the alkali load of the material, which suggests that potassium-rich additives could be useful in reducing the tar content of the raw gas in gasifiers. An advantage of this measure is that it is simple to apply in an existing unit. However, the consequences for corrosion, agglomeration, and the fluidization properties of the bed need to be investigated.

In the present investigation, the catalytic conversion of the tar species was more effective when active bed materials were used in the gasifier, as compared to employing a downstream catalytic reformer. The general differences observed between these two approaches may be explained by a combination of two factors: (1) the type of tar species to which the catalyst is exposed, as suggested by Corella and co-workers [46]; and/or (2) the differences between the activities of the materials tested. The catalytic activity of the material used in a gasification test is different from that of the same material used in a reformer test. Gasification tests usually take more time (e.g., continuous run over days/weeks) and the catalysts benefit from longer time to activate, which is exacerbated by exposure of the catalyst to fuel ash inside the gasifier [50, 62]. Therefore, improved tar removal capacity is anticipated for feldspar when it is applied as an *in situ* catalyst, as compared to its application in the downstream reformer (as in the present study).

The results presented here indicate that the chemical interactions between the bed material and the fuel exert a major influence on the degree of conversion of the char, whereas the impact on char conversion of the residence time of the fuel is limited. The rate of steam gasification of char seems to be enhanced by catalytic species released by the bed material in the gasifier, and the catalytically active species may be a releasable form of alkali, as observed previously [49]. The positive effect of oxygen-carrying capacity on char conversion seems to be relevant only at high levels of oxygen transport, such as those pertaining to CLC units (i.e.,  $\phi > 1$ ). Therefore, the kinetics of alkali release by the bed material and that of uptake of alkali by the char particles become key elements in understanding catalytic steam gasification of char with in-bed catalysts.

The limited impact of fluid dynamics on fuel conversion suggests that a simple gasifier design can yield high degree of fuel conversion if the bed material has a high level of catalytic activity. Two important findings support this idea: (1) at least 44% of the volatiles are in contact with the bed material under conditions where fuel segregation prevails, i.e., the fuel is gravity-fed into a mildly fluidized bed. This fair degree of gas-solid mixing enables the heterogeneous catalysis of steam-reforming reactions by the bed material; and (2) catalytic species are released into the gaseous phase in a gasification environment. If the tar reactions can be catalyzed homogeneously by gaseous alkali species, the gas-solid contacts do not limit the degree of tar conversion. Therefore, having a freeboard that has a complex shape in order to enhance gas-solid mixing or using in-bed fuel feeding may not be important to attain high-level conversion of tar species. Moreover, over-bed fuel feeding is simpler, more reliable, and more economical than in-bed fuel feeding. For instance, in-bed fuel feeding entails operational challenges related

to uncontrolled heating caused by the nearby hot bed material, resulting in partial devolatilization of the fuel that is already in the feeding system [12]. Instead, for reducing the tar load of the raw gas, the availability of the gaseous catalyst in the gasifier becomes crucial.

The main technical challenge for the biomass gasification technology continues to be the incomplete conversion of problematic hydrocarbons into non-condensable species. The stringency of the control of the production of tar determines whether the gasification plant can be run continuously and whether starting-up/sustaining of the operation is feasible. Based on experience with the Chalmers gasifier, the key to achieving a high level of conversion of hydrocarbons is to enhance the kinetics of tar decomposition by catalytic means, which requires a good understanding of catalyst activity and functioning. Further knowledge of these topics will confirm the technical feasibility of large-scale production of syngas from renewable sources by improving the reliability of the gasifier. Within a favorable economic and political framework, a reliable biomass gasification technology could partially replace or complement traditional syngas production, which involves steam reforming of fossil feedstocks. This would provide the means to increase the share of renewable sources in a wide range of industries where syngas is currently used as intermediate, e.g., the chemical industry, refineries, ammonia synthesis plants etc.

## 6 - Conclusions

---

In this thesis, strategies to control the degree of fuel conversion in dual fluidized bed (DFB) gasifiers were investigated experimentally in a 2–4-MW<sub>th</sub> DFB gasifier. The work was mainly exploratory, and it covered both fluid-dynamic (i.e., residence time, fluidization) and chemical aspects (i.e., temperature, active bed materials) of biomass conversion in DFB gasifiers. The main conclusions of this work are:

- The most effective of the tested measures to enhance fuel conversion is the use of catalytic bed materials in the DFB, as the kinetics of char gasification and steam reforming of tar are both slow.
- Fluid dynamics play a secondary role in the DFB steam gasifier, provided that the bed is well-fluidized. With over-bed feeding of biomass, good fluidization and fuel mixing are assured at fluidization values of approximately  $u_o/u_{mf} > 5-6$ .
- When activated, natural bed materials, such as olivine, provide high level of activity for steam reforming of hydrocarbons, yielding significantly higher rates of hydrocarbon decomposition. Under the conditions tested, the yield of total condensable species was halved by activated olivine, as compared to a similar case with inert sand as the bed material, and the yield of heavier tar compounds (i.e., heavier than BTX) was reduced 3.5-fold.
- Inorganic impurities in the fuel composition, such as potassium, enhance catalyst performance for tar reforming, the WGS reaction, and steam gasification of char. The relative contributions of the ash species to the net activity of the bed material are, however, difficult to measure, and the catalytic mechanism associated with the ash layers coating the particles remains unknown.

Overall, this work shows that the choice of catalyst and the optimization of its activity are the key elements in achieving efficient conversion of tar species, thereby unlocking the main technical challenge of biomass gasification (i.e., tar formation). To increase the reliability of the biomass-to-syngas process and its competitiveness in relation to conventional steam reforming of naphtha/natural gas, additional knowledge is needed in relation to: (1) the activation process; (2) the functioning of the catalyst; and (3) the mechanism underlying the catalytic decomposition of tar.



## 7 - Future work

---

In line with the main conclusions drawn in this thesis, future studies should focus on characterizing and optimizing the activities of the bed materials. The relationship between bed material activity and the mechanism of hydrocarbon conversion must be addressed. Resolving the following research issues contribute to the reliability of biomass gasification, with the ultimate aim of providing a competitive alternative to the traditional route for syngas production:

- Elucidate the relevance of homogeneous catalysis in the steam reforming of hydrocarbons. The findings would shed light on the relative shares of homogeneous and heterogeneous catalysis in the steam reforming of hydrocarbons, when fuel-ash elements, and particularly alkali species, are involved.
- Optimize the activities of the bed materials by means of additives, and understand the catalytic route for tar decomposition. The focus should be on the potential to control the hydrocarbon yield by exploiting the trade-off between the temperature and the activity of the bed material. This strategy could be useful for controlling the total yield of tar, as well as its composition (i.e., heavier aromatics vs lighter tar).

Furthermore, based on the results obtained from testing feldspar in a downstream reformer, an investigation of the catalytic activity of feldspar for tar species when used as an in-bed catalyst is warranted. Scrutinizing the tar spectrum of samples collected during in-bed and downstream reformer tests might give insights into the tar decomposition mechanism that operates when the catalyst is used in-bed, as compared to downstream of the gasifier.





## 8 - References

---

1. Rostrup-Nielsen, J. and L.J. Christiansen, *Concepts in syngas manufacture*. Vol. 10. 2011: World Scientific.
2. Rostrup-Nielsen, J.R., *Catalytic steam reforming*, in *Catalysis*. 1984, Springer. p. 1-117.
3. Rostrup-Nielsen, J.R., *Syngas in perspective*. *Catalysis today*, 2002. **71**(3): p. 243-247.
4. Moud, P.H., et al., *Effect of gas phase alkali species on tar reforming catalyst performance: Initial characterization and method development*. *Fuel*, 2015. **154**: p. 95-106.
5. Alstrup, I., J.R. Rostrup-Nielsen, and S. Røen, *High temperature hydrogen sulfide chemisorption on nickel catalysts*. *Applied Catalysis*, 1981. **1**(5): p. 303-314.
6. Lundberg, L., et al., *Determination of Kinetic Parameters for the Gasification of Biomass Char Using a Bubbling Fluidized Bed Reactor*, in *22nd International Conference on Fluidized Bed Conversion*. 2015: Turku, Finland.
7. Larsson, A., *Fuel conversion in a dual fluidized bed gasifier*, in *Department of Energy and Environment*. 2014, Chalmers University of Technology: Gothenburg, Sweden.
8. Evans, R.J. and T.A. Milne, *Molecular characterization of the pyrolysis of biomass*. *Energy & Fuels*, 1987. **1**(2): p. 123-137.
9. Milne, T.A., N. Abatzoglou, and R.J. Evans, *Biomass gasifier" tars": Their nature, formation, and conversion*. Vol. 570. 1998: National Renewable Energy Laboratory Golden, CO.
10. Abdoulmoumine, N., et al., *A review on biomass gasification syngas cleanup*. *Applied Energy*, 2015. **155**: p. 294-307.
11. Kiel, J., et al., *Primary measures to reduce tar formation in fluidised-bed biomass gasifiers*. *ECN*, ECN-C-04-014, 2004.
12. Thunman, H., A. Larsson, and M. Hedenskog, *Commissioning of the GoBiGas 20MW Bio-methane Plant*, in *tcbiomass2015*. 2015: Chicago.
13. Pfeifer, C., R. Rauch, and H. Hofbauer, *In-Bed Catalytic Tar Reduction in a Dual Fluidized Bed Biomass Steam Gasifier*. *Industrial & Engineering Chemistry Research*, 2004. **43**(7): p. 1634-1640.
14. Zhang, J., et al., *Recent studies on chemical engineering fundamentals for fuel pyrolysis and gasification in dual fluidized bed*. *Industrial & Engineering Chemistry Research*, 2013. **52**(19): p. 6283-6302.
15. Sehested, J., *Four challenges for nickel steam-reforming catalysts*. *Catalysis Today*, 2006. **111**(1-2): p. 103-110.
16. Pfeifer, C., et al., *Next generation biomass gasifier*, in *Proc. 19th European Biomass Conference and Exhibition*. 2011: Berlin, Germany.
17. Wilk, V., J.C. Schmid, and H. Hofbauer, *Influence of fuel feeding positions on gasification in dual fluidized bed gasifiers*. *Biomass and Bioenergy*, 2013. **54**(0).
18. Zhang, Y., B. Jin, and W. Zhong, *Experimental investigation on mixing and segregation behavior of biomass particle in fluidized bed*. *Chemical Engineering and Processing: Process Intensification*, 2009. **48**(3): p. 745-754.

19. Kunii, D. and O. Levenspiel, *Fluidization Engineering (Second Edition)*. 1991, Boston: Butterworth-Heinemann. 61-94.
20. Gómez-Barea, A. and B. Leckner, *Modeling of biomass gasification in fluidized bed*. Progress in Energy and Combustion Science, 2010. **36**(4): p. 444-509.
21. Lv, D., et al., *Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification*. Fuel Processing Technology, 2010. **91**(8): p. 903-909.
22. Fuentes-Cano, D., et al., *The influence of temperature and steam on the yields of tar and light hydrocarbon compounds during devolatilization of dried sewage sludge in a fluidized bed*. Fuel, 2013. **108**: p. 341-350.
23. de Andrés, J.M., A. Narros, and M.E. Rodríguez, *Behaviour of dolomite, olivine and alumina as primary catalysts in air-steam gasification of sewage sludge*. Fuel, 2011. **90**(2): p. 521-527.
24. Sutton, D., B. Kelleher, and J.R.H. Ross, *Review of literature on catalysts for biomass gasification*. Fuel Processing Technology, 2001. **73**(3): p. 155-173.
25. Devi, L., K.J. Ptasinski, and F.J.J.G. Janssen, *A review of the primary measures for tar elimination in biomass gasification processes*. Biomass and Bioenergy, 2003. **24**(2): p. 125-140.
26. Rowe, P.N. and A.W. Nienow, *Particle mixing and segregation in gas fluidised beds. A review*. Powder Technology, 1976. **15**(2): p. 141-147.
27. Fiorentino, M., A. Marzocchella, and P. Salatino, *Segregation of fuel particles and volatile matter during devolatilization in a fluidized bed reactor-II. Experimental*. Chemical Engineering Science, 1997. **52**(12): p. 1909-1922.
28. Solimene, R., A. Marzocchella, and P. Salatino, *Hydrodynamic interaction between a coarse gas-emitting particle and a gas fluidized bed of finer solids*. Powder Technology, 2003. **133**(1-3): p. 79-90.
29. Olsson, J., D. Pallarès, and F. Johnsson, *Lateral fuel dispersion in a large-scale bubbling fluidized bed*. Chemical Engineering Science, 2012. **74**: p. 148-159.
30. Einstein, A., *Investigations on the Theory of the Brownian Movement*. 1956, USA: Dover Publications, Inc.
31. Niklasson, F., et al., *Estimation of Solids Mixing in a Fluidized-Bed Combustor*. Industrial & Engineering Chemistry Research, 2002. **41**(18): p. 4663-4673.
32. Sette, E., D. Pallarès, and F. Johnsson, *Experimental quantification of lateral mixing of fuels in fluid-dynamically down-scaled bubbling beds*. Applied Energy, 2014. **136**(0): p. 671-681.
33. Sette, E., D. Pallarès, and F. Johnsson, *Influence of bulk solids cross-flow on lateral mixing of fuel in dual fluidized beds*. Fuel Processing Technology, 2015. **140**: p. 245-251.
34. Larsson, A., et al., *Evaluation of Performance of Industrial-Scale Dual Fluidized Bed Gasifiers Using the Chalmers 2-4-MWth Gasifier*. Energy & Fuels, 2013. **27**(11).
35. Herguido, J., J. Corella, and J. Gonzalez-Saiz, *Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot scale. Effect of the type of feedstock*. Industrial & Engineering Chemistry Research, 1992. **31**(5): p. 1274-1282.

36. Elliott, D.C., *Relation of Reaction Time and Temperature to Chemical Composition of Pyrolysis Oils*, in *Pyrolysis Oils from Biomass*. 1988, American Chemical Society. p. 55-65.
37. Ming, Q., et al., *Steam reforming of hydrocarbon fuels*. *Catalysis Today*, 2002. **77**(1-2): p. 51-64.
38. Rauch, R., et al. *Comparison of different olivines for biomass steam gasification*. in *Conference for Science in Thermal and Chemical Biomass Conversion*. 2004.
39. Almansa, G.A., et al., *ECN System for Methanation (ESME)*, in *EUBCE 2015* 2015: Vienna, Austria
40. Adánez, J., et al., *Ilmenite Activation during Consecutive Redox Cycles in Chemical-Looping Combustion*. *Energy & Fuels*, 2010. **24**(2): p. 1402-1413.
41. Azhar Uddin, M., et al., *Catalytic decomposition of biomass tars with iron oxide catalysts*. *Fuel*, 2008. **87**(4-5): p. 451-459.
42. Nordgreen, T., T. Liliedahl, and K. Sjöström, *Metallic iron as a tar breakdown catalyst related to atmospheric, fluidised bed gasification of biomass*. *Fuel*, 2006. **85**(5-6): p. 689-694.
43. Virginie, M., et al., *Effect of Fe-olivine on the tar content during biomass gasification in a dual fluidized bed*. *Applied Catalysis B: Environmental*, 2012. **121-122**(0): p. 214-222.
44. Pfeifer, C., S. Koppatz, and H. Hofbauer, *Steam gasification of various feedstocks at a dual fluidised bed gasifier: Impacts of operation conditions and bed materials*. *Biomass Conversion and Biorefinery*, 2011. **1**(1): p. 39-53.
45. Larsson, A., et al., *Using Ilmenite To Reduce the Tar Yield in a Dual Fluidized Bed Gasification System*. *Energy & Fuels*, 2014. **28**(4): p. 2632-2644.
46. Corella, J., et al., *Biomass Gasification in Fluidized Bed: Where To Locate the Dolomite To Improve Gasification?* *Energy & Fuels*, 1999. **13**(6): p. 1122-1127.
47. Vassilev, S.V., et al., *An overview of the chemical composition of biomass*. *Fuel*, 2010. **89**(5): p. 913-933.
48. Niu, Y., H. Tan, and S.e. Hui, *Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures*. *Progress in Energy and Combustion Science*, 2016. **52**: p. 1-61.
49. Keller, M., H. Leion, and T. Mattisson, *Mechanisms of Solid Fuel Conversion by Chemical-Looping Combustion (CLC) using Manganese Ore: Catalytic Gasification by Potassium Compounds*. *Energy Technology*, 2013. **1**(4): p. 273-282.
50. Kirnbauer, F., et al., *The positive effects of bed material coating on tar reduction in a dual fluidized bed gasifier*. *Fuel*, 2012. **95**: p. 553-562.
51. Marinkovic, J., et al., *Characteristics of olivine as a bed material in an indirect biomass gasifier*. *Chemical Engineering Journal*, 2015. **279**: p. 555-566.
52. Wang, L., et al. *A critical review on additives to reduce ash related operation problems in biomass combustion applications*. in *Technoport 2012 - Sharing Possibilities and 2nd Renewable Energy Research Conference (RERC2012)*. 2012.
53. Grootjes, A.J., van der Meijden, C.M., Visser, H.J.M., van der Drift, A., *Improved Gasifier Availability with Bed Material and Additives*, in *21st European Biomass Conference and Exhibition*. 2013. p. 407 - 413.

54. Kirnbauer, F., et al., *Behavior of inorganic matter in a dual fluidized steam gasification plant*. Energy & Fuels, 2013. **27**(6): p. 3316-3331.
55. Marinkovic, J., et al., *Impact of Biomass Ash-Bauxite Bed Interactions on an Indirect Biomass Gasifier*. Energy & Fuels, 2016. **30**(5): p. 4044-4052.
56. Punjak, W.A., M. Uberoi, and F. Shadman, *High-temperature adsorption of alkali vapors on solid sorbents*. AIChE Journal, 1989. **35**(7): p. 1186-1194.
57. Boström, D., et al., *Ash Transformation Chemistry during Combustion of Biomass*. Energy & Fuels, 2012. **26**(1): p. 85-93.
58. Frandsen, F.J., *Ash formation, deposition and corrosion when utilizing straw for heat and power production*, in Department of Chemical and Biochemical Engineering. 2011, Technical University of Denmark.
59. Zevenhoven, M., P. Yrjas, and M. Hupa, *Ash-Forming Matter and Ash-Related Problems*, in *Handbook of Combustion*. 2010, Wiley-VCH Verlag GmbH & Co. KGaA.
60. Kirnbauer, F. and H. Hofbauer, *The mechanism of bed material coating in dual fluidized bed biomass steam gasification plants and its impact on plant optimization*. Powder Technology, 2013. **245**: p. 94-104.
61. Kuba, M., et al., *Deposit build-up and ash behavior in dual fluid bed steam gasification of logging residues in an industrial power plant*. Fuel Processing Technology, 2015. **139**: p. 33-41.
62. Marinkovic, J., *Choice of bed material: a critical parameter in the optimization of dual fluidized bed systems*, in *Energy and Environment*. 2016, Chalmers University of Technology.
63. Cuadrat, A., et al., *Behavior of ilmenite as oxygen carrier in chemical-looping combustion*. Fuel Processing Technology, 2012. **94**(1): p. 101-112.
64. Pecho, J., et al., *Reactive bed materials for improved biomass gasification in a circulating fluidised bed reactor*. Chemical Engineering Science, 2008. **63**(9): p. 2465-2476.
65. Mendiara, T., et al., *Biomass combustion in a CLC system using an iron ore as an oxygen carrier*. International Journal of Greenhouse Gas Control, 2013. **19**(0): p. 322-330.
66. Keller, M., et al., *Gasification inhibition in chemical-looping combustion with solid fuels*. Combustion and Flame, 2011. **158**(3): p. 393-400.
67. Fushimi, C., T. Wada, and A. Tsutsumi, *Inhibition of steam gasification of biomass char by hydrogen and tar*. Biomass and Bioenergy, 2011. **35**(1): p. 179-185.
68. Brage, C., et al., *Use of amino phase adsorbent for biomass tar sampling and separation*. Fuel, 1997. **76**(2): p. 137-142.
69. Israelsson, M., M. Seemann, and H. Thunman, *Assessment of the Solid-Phase Adsorption Method for Sampling Biomass-Derived Tar in Industrial Environments*. Energy & Fuels, 2013. **27**(12): p. 7569-7578.
70. Israelsson, M., A. Larsson, and H. Thunman, *Online Measurement of Elemental Yields, Oxygen Transport, Condensable Compounds, and Heating Values in Gasification Systems*. Energy & Fuels, 2014. **28**(9): p. 5892-5901.
71. Neves, D., et al., *Method for online measurement of the CHON composition of raw gas from biomass gasifier*. Applied Energy, 2014. **113**(0): p. 932-945.

72. Leion, H., T. Mattisson, and A. Lyngfelt, *Solid fuels in chemical-looping combustion*. International Journal of Greenhouse Gas Control, 2008. **2**(2): p. 180-193.
73. Cuadrat, A., et al., *The use of ilmenite as oxygen-carrier in a 500kWth Chemical-Looping Coal Combustion unit*. International Journal of Greenhouse Gas Control, 2011. **5**: p. 1630-1642.