

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

## Carbon Recovery in A Dual Fluidized Bed Gasifier

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# Abstract

As the concept of a circular economy gains acceptance and awareness of climate change and its disastrous consequences increases, the ways in which we produce the carbon-based goods upon which so much of our economy depends need to change. Society must end its reliance on fossil carbon resources and shift to renewable sources that enable the establishment of a carbon cycle. Plastic and biogenic wastes should become our main sources of carbon for new materials. This would simultaneously address the critical issues related to the current deficit of recycling and robust collection systems, which currently entails immense loss of value and represents a threat to the environment. The biomass waste would also compensate for inevitable leakage from the carbon cycle and enable overall-negative CO<sub>2</sub> emissions.

Technologies are needed that are capable of extracting efficiently the carbon from these new sources. This will be challenging given the expected heterogeneous nature of such sources. In this context, the Dual Fluidized Bed (DFB) gasification process is an attractive technology owing to its flexibility. This thesis investigates the possibility for carbon recovery in DFB gasification processes. The various configurations in which a DFB gasification unit can be designed and operated are discussed, with respect to their carbon balances. In addition, as the valorization of waste materials is a critical aspect of the circular economy, the use of such materials in DFB processes, beyond the consideration of carbon extraction, is considered. These materials may possess properties that can enhance the carbon recovery of the existing process or around which an entire process can be devised.

To illustrate the challenges related to optimizing carbon recovery in DFB gasification processes, and the possible uses and impacts of waste materials in those processes, experiments were carried out in the Chalmers University of Technology DFB gasifier. The first set of experiments was aimed at increasing carbon recovery in the form of valuable products in a regular DFB gasifier by increasing the catalytic activity of the bed towards the reforming of non-valuable compounds, in this case tar. This was achieved by circulating the flue gas ash, which is a waste material produced by the process, back into the system. The second set of experiments was designed to investigate the feasibility and carbon balance of Chemical-Looping Gasification (CLG), which is a DFB gasification technology whereby an oxygen carrier produces the heat needed for the gasification reaction. The CLG technology, which potentially enables carbon recovery into a single, undiluted stream, was explored for two cases. The first case involved CLG of biomass using a waste from the steel-making industry as the oxygen carrier. The second case entailed CLG of Automotive Shredder Residue (ASR), a plastic-containing waste the high ash content of which leads to the formation of an oxygen-carrying bed material.

The results presented in this thesis reveal that the fate of the CO<sub>2</sub> in the raw gas is a critical issue, both in regular DFB gasification with an active bed and in CLG. As the activity of the bed material increases, as achieved by circulating the flue gas ash, the carbon is transferred from both non-valuable and valuable products to CO<sub>2</sub> in the raw gas, owing to the action of the water-gas shift. In the case of CLG, the oxygen transport from the bed material results in significant oxidation of H<sub>2</sub> and CO, predominantly, thereby transferring carbon to CO<sub>2</sub>, which becomes the main carbon output from the process. However, the oxygen transport is also identified as the key parameter for solving a crucial issue in CLG, i.e., the achievement of complete conversion of the fuel in the fuel reactor. The gasification of ASR in the Chalmers gasifier led to an oxygen-carrying bed, which may facilitate operation in CLG mode, provided that the oxygen transport level is increased. The possibilities to achieve this are discussed in this thesis.

In terms of the selection and operation of DFB gasification processes, the results of this work have the following implications: (i) for regular DFB gasification, the catalytic activity and temperature levels should be carefully selected, based on the comparison of the energy cost of separation of the CO<sub>2</sub> from the raw gas on the one hand, and the destruction or valorization of non-valuable products on the other hand; and (ii) for CLG, the process should be designed to maximize the conversion of the fuel in the fuel reactor, while minimizing the oxidation of the raw gas. The viability of CLG in terms of producing simultaneously chemical precursors and CO<sub>2</sub> that is ready for sequestration should be assessed by comparing with the alternative process, i.e., DFB gasification with oxyfuel combustion.

## Acknowledgements

This PhD journey has so far been an extremely enriching one and, at time, a challenging one. I have been lucky to have great people guide me and accompany me on the path. I would, therefore, like to first thank my main supervisor, Martin Seemann, for being always eager to discuss work-related and non-work-related topics, for his constant humor, and for maintaining a research group with such a great atmosphere. I would also like to thank my co-supervisor, Henrik Thunman, for his guidance and support, and for his ability to make me understand better the greater picture.

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# List of Publications

This thesis is based on the work presented in the following papers:

## Paper I

Pissot, S., Berdugo Vilches, T., Thunman, H., & Seemann, M.

Effect of ash circulation on the performance of a dual fluidized bed gasification system

*Biomass and Bioenergy*, 115, 45–55

## Paper II

Pissot, S., Berdugo Vilches, T., Maric, J., Cañete Vela, I., Thunman, H., & Seemann, M.

Thermochemical Recycling of Automotive Shredder Residue by Chemical-Looping Gasification Using the Generated Ash as Oxygen Carrier

*Energy & Fuels*, 33, 11552-11566

## Paper A

Pissot, S., Berdugo Vilches, T., Maric, J., & Seemann, M.

Chemical looping gasification in a 2-4 MWth dual fluidized bed gasifier

*23rd International Conference on Fluidized Bed Conversion*  
*Seoul, South Korea, 2018-05-13 - 2018-05-17*

## List of Peer-Reviewed Publications Not Included in this Thesis

Thunman, H., Berdugo Vilches, T., Seemann, M., Maric, J., Vela, I. C., Pissot, S., & Nguyen, H. N. T. (2019)

Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery.

*Sustainable Materials and Technologies*, 22

Maric, J., Berdugo Vilches, T., Pissot, S., Cañete Vela, I., Gyllenhammar, M., & Seemann, M. (2020)

Emissions of dioxins and furans during steam gasification of Automotive Shredder residue; experiences from the Chalmers 2–4-MW indirect gasifier

*Waste Management*, 102, 114–121

## List of Abbreviations

AAEM: Alkali and alkali-earth metals

AR: Air reactor

ASR: Automotive shredder residue

ASU: Air separation unit

BTX: Benzene, Toluene and Xylene

CFB: Circulating fluidized bed

CGE: Cold gas efficiency

CLC: Chemical-looping combustion

CLG: Chemical-looping gasification

DFB: Dual fluidized bed

GC: Gas chromatograph

HD: Heat demand

HO: Heat output

HTR: High-temperature reactor

OCAC: Oxygen carrier-aided combustion

POP: Persistent organic pollutants

SPA: Solid-phase adsorption

TGA: Thermogravimetric analysis

TOC: Total organic compounds

WGS: Water-gas shift

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# Introduction

Our planet represents a finite environment, with extensive, yet limited resources and a limited resilience to the changes caused by unbridled human activity. Awareness of this predicament has grown in the recent years. It is now evident that radical changes in our production and consumption systems, as well as our behaviors are needed if we are to meet the challenges of increasing industrialization worldwide, a growing population, and developments in life quality. These changes are crucial to limiting resource exhaustion and avoiding dramatic climate change consequences. As a response to these issues, the concept of the circular economy has become increasingly popular. The circular economy, which is not limited to materials aspects, envisions a system that creates value from the economic, societal, and environmental perspectives [1,2]. Nonetheless, creating a circular path for products that today mostly end up as waste is one of the cornerstones of this concept. Simply put, material streams that are currently regarded as waste that has to be disposed of can no longer be considered as such. Instead, these materials should be re-used, for their originally intended purpose or in another way, or transformed into other valuable products.

In addition to the issue of resource management, the disposal of waste into the environment, with little concern for its fate or its impact, causes serious problems. The disposal of one type of waste in particular, CO<sub>2</sub>, by release into the atmosphere, has led to and is continuously leading to climate change [3], the dire consequences of which are each year becoming more evident. Consequently, minimization of CO<sub>2</sub> emission to the atmosphere is essential to ensure that the consequences do not endanger the wellbeing, and even the survival, of future generations. However, our entire industrial sector is based on the idea that CO<sub>2</sub> can be dumped in the atmosphere at a low cost. Therefore, radical changes in industrial and societal practices and attitudes are required. Decarbonization solutions for energy production, manufacturing, and transportation must be devised, and the existing ones must be improved. Carbon capture and storage or utilization needs to be implemented at the global scale, to reverse actively the trend in atmospheric CO<sub>2</sub> concentration. Finally, an end must be put to the dependency on fossil-based carbon sources, since they result in a net addition of carbon to the environment.

Nevertheless, this creates a problem when considering carbon-based products upon which our society depends heavily. Indeed, while the energy and transportation sectors can be decarbonized, carbon sources are obviously needed to produce a wide range of our everyday products. However, renewable carbon sources are limited to biomass, carbon-based anthropogenic waste, and CO<sub>2</sub> from direct air capture. The latter is limited by the energy cost of separating CO<sub>2</sub>. Besides, producing materials from atmospheric carbon may incentivize releasing carbon to the atmosphere as part of the carbon cycle rather than behaviors that avoid any carbon slippage to the environment. Supplying the world's demand for carbon using exclusively biomass is not realistic, as it involves a variety of ecological, economical, and societal issues. For instance, a high demand for energy crops could endanger biodiversity through overexploitation and the introduction of non-indigenous crops. Moreover, energy crops may compete with food crops for land, which could lead to local food supply problems, driving up food prices.

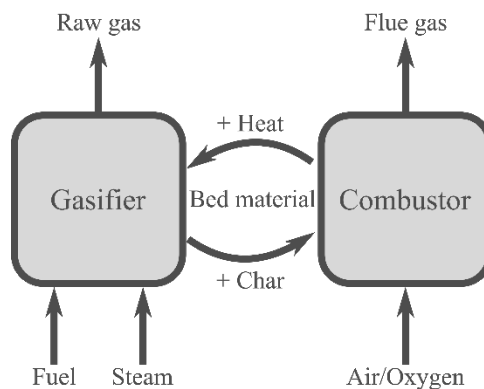
The use of carbon-based anthropogenic waste, which mainly consists of plastic waste, would address many of the issues related to the current lack of recycling of such waste. Notably, plastic waste has become an environmental threat, mainly because of the scale of plastic production, the propensity of plastic to leak into the environment exacerbated by a throwaway culture, and the lack of plastic collection systems in many countries. For instance, Jambeck *et al.* have estimated that, for Year 2010,

99.5 Mt of plastic waste was generated in coastal regions of the world (including populations living within 50 km of a coast), 31.9 Mt of which was classified as “mismanaged”, and 4.8 to 12.7 Mt of this waste entered the oceans [4]. Therefore, it is clear that using plastic waste as the main carbon source would impose a value on plastic waste collection and, thereby, limit the leakage of plastic into the environment. Despite the aforementioned issues, biomass would still have a role to play in the carbon cycle. Biomass waste could indeed be used to supply carbon to compensate for the inevitable losses from the plastic cycle, and to address the increasing demand for carbon.

The extraction of carbon from waste using thermochemical methods will be the preferred pathway for establishing the carbon cycle. When it comes to plastic waste, mechanical recycling can at first glance seem like the more logical approach, given that its aim is to restore the plastic to its original use with limited energy expenditure. However, mechanical recycling is only suitable for highly homogeneous plastic waste streams, and, even then, some loss in quality of the newly formed plastic is inevitable. Unfortunately, the overwhelming majority of plastic waste is expected to be in the form of complex mixtures of polymers. Mechanical recycling of such mixtures is extremely complex, due to differences in melting points, processing temperatures, and the potential immiscibility of the melt formed [5]. Obtaining single-polymer streams for mechanical recycling is also challenging, and the presence of multiple additives [6] makes obtaining a “pure” stream impossible. To make matters worse, during mechanical recycling, thermal-mechanical degradation occurs, which when added to the degradation that occurs during the lifetime of a plastic product, results in a product with compromised properties [5]. For these reasons, thermochemical recycling of plastic waste into molecular building blocks is preferable. Moreover, this enables flexibility in the distribution of carbon into the various end-products and makes the carbon cycle adaptable to changes in production and consumption patterns.

However, these new carbon sources are more challenging than the fossil sources that we have relied upon to date. Indeed, plastic and biomass wastes are expected to be more heterogeneous, often comprising a mixture of plastic and biogenic wastes, as well as inorganic waste, such as metals. These wastes often contain elements that can lead to the formation of pollutants during their thermochemical reprocessing. Thus, the selection of an optimal operational window will be challenging, as optimal conversion of the various polymers or biomass types may occur at different temperatures. The variety of inorganics may lead to operational issues in the thermochemical reactor and within its cooling sections. Therefore, a thermochemical recycling technology that is sufficiently robust to handle these issues is required.

In this context, Dual Fluidized Bed (DFB) gasification has certain features that makes it a strong candidate as the central technology in the carbon cycle. The DFB technology is analogous to the Fluid Catalytic Cracking technology employed in the petroleum industry to crack gas oil, with the difference that it converts solid fuels. A DFB gasification system consists of two interconnected fluidized bed reactors, as illustrated in Figure 1. One reactor is a fluidized bed gasifier, usually operated as a bubbling bed, in which thermochemical breakdown of the fuel takes place in the presence of steam. The other reactor is a Circulating Fluidized Bed (CFB) combustor, which burns the fraction of the fuel that was not converted in the gasifier, so as to provide the heat required by the gasifier. The heat is transferred from the combustor to the gasifier by a bed material that circulates between the two reactors. The separation of the combustion reaction from the gasification reactions leads to a concentrated product gas, without the need to produce pure oxygen, as is the case for direct gasification technologies.



**Figure 1.** Dual fluidized bed gasification setup.

The DFB gasification technology is particularly well suited to the conversion of waste streams. The use of a fluidized bed ensures homogeneous temperature profiles within both reactors, thereby avoiding hotspots and facilitating operational control of the reactions. The high heating rates ensure a high throughput. DFB reactors require little fuel preparation beyond drying, which makes them extremely flexible. Conversion of the waste in the weakly oxidative environment of the gasifier may be conducive to generating lower levels of emissions of, for instance, dioxins and polychlorinated dibenzofurans [7]. The char that is burnt in the combustor is highly reactive and contains few impurities compared with the parent fuel, which leads to low levels of emissions in the flue gases. In addition, the bed material can easily incorporate additives, which reduce emissions by acting as sorbents or catalysts. Similarly, catalysts that act to adjust the gas composition in the gasifier can be incorporated. These catalysts will be continuously regenerated in the combustor.

In addition, DFB gasification offers great flexibility regarding carbon recovery. The carbon distribution into the products of the gasifier can, to a large extent, be tailored to requirements by adjusting the reactor temperature and the residence time of the fuel. The distribution of carbon between the two reactors can be adjusted, for instance by supplying part of the heat with electricity, thus shifting more carbon to the gasifier. The use of oxygen-enriched air in the combustor increases the  $\text{CO}_2$  concentration to levels that make the sequestration of that carbon viable. Taking this approach to its extreme, i.e., operating the combustor as an oxyfuel combustor, produces a flue gas that is rich in  $\text{CO}_2$  and that needs little additional processing for sequestration of the carbon. The carbon recovery as  $\text{CO}_2$  in the raw gas can also be fine-tuned, which adds another pure  $\text{CO}_2$  stream that is ready for sequestration, once the  $\text{CO}_2$  has been scrubbed from the raw gas. If plastic waste is the main carbon source being converted, biomass can then be added to make the process carbon-negative. Overall, DFB gasification offers flexibility in the valorization of the carbon, which is necessary for the circular carbon economy to adjust rapidly to changes in consumption and regulations.

Nonetheless, despite its promising features, DFB gasification has not yet been implemented at commercial scale. Only a few plants exist at large scale: the 8-MW unit in Güssing, Austria [8], upon which are based the 16-MW Senden plant in Germany [9] and the 32-MW GoBiGas plant [10] in Gothenburg, Sweden, and the TIGAR gasifier, which converts 15 MW of lignin, designed and operated by the IHI Corporation in Yokohama, Japan [11]. Furthermore, the conversion of plastic waste in DFB gasifiers at semi-industrial [12] or pilot scale [13] is also currently limited. In addition, carbon distribution and recovery have not been in focus in those studies. There is, therefore, a need to develop novel ways of exploring DFB gasification and its potential as part of the carbon cycle.

This thesis discusses the carbon distribution in a DFB gasification system and the possibilities it offers for enhancing carbon recovery, based on the results of three scientific articles, two of which have been published (**Papers I and II**) and one that is an unpublished conference article (**Paper A**). In line with the principle of the circular economy, the possibilities for using waste streams at various levels in a DFB gasification process are discussed. The discussion in this thesis goes beyond the classical design of a DFB gasifier. Processes that decarbonize the heat generation step and processes that concentrate the CO<sub>2</sub> streams are also discussed. The overarching objective of this work is to contribute to the knowledge on the DFB gasification technology and to strengthen its standing as a carbon-extraction technology in the circular economy.

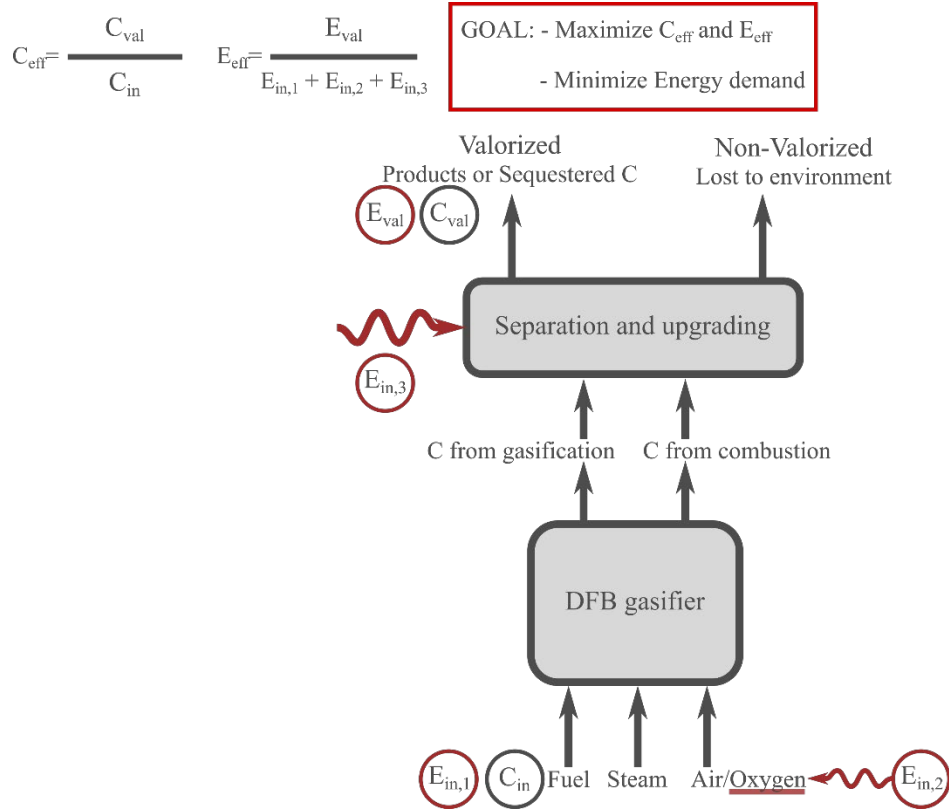
# Chapter 1: Enhancing carbon recovery in DFB processes

## 1.1. Carbon distribution in a DFB gasification system

Strengthening the status of the DFB gasification technology in the circular economy entails maximizing both its carbon extraction efficiency and its energy efficiency, as well as minimizing its energy demand, as shown in Figure 2. While complete carbon efficiency could be achieved for many processes if unlimited energy is introduced into the system, this is hardly in line with the ethos of the circular economy, in which the parsimonious use of resources, including energy, is paramount. In the DFB gasification technology, the carbon introduced with the fuel fed to the gasification reactor and, potentially, to the combustor exits the reactor in two streams. These two streams then undergo a series of separation and upgrading steps, wherein the various species are separated and further reacted to obtain products that meet the requirements of, for instance, a downstream synthesis step.

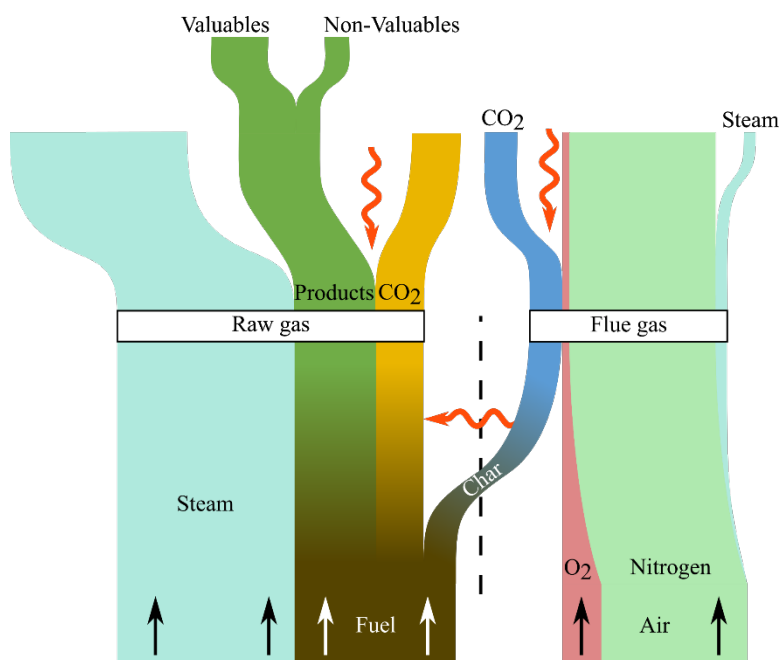
Regarding the flue gas stream, the carbon, which is in the form of  $\text{CO}_2$ , may or may not be separated from the combustion air. This choice regarding separation will be based on the  $\text{CO}_2$  concentration and, thereby, the energy cost of the separation process. Oxyfuel combustion can be employed to alleviate this cost and render the separation straightforward. Choosing this technology over air combustion will require an energy cost comparison of the processes of pure oxygen production and the separation of the  $\text{CO}_2$  from the amine scrubbing agent. Regardless of the way it is separated, the  $\text{CO}_2$  may be sequestered to contribute to mitigating the emissions of the plant or even making them negative, or it may be reacted to form products. Conversely, it may be emitted to the atmosphere.

The carbon efficiency of the DFB gasification process is reflected in the ratio of the carbon valorized, i.e., recovered as valuable products after upgrading or sequestration, to the carbon fed into the DFB. If carbon is introduced into the upgrading section, it must be accounted for in the input to the DFB process. Similarly, the energy efficiency is the ratio of the energy in the valorized products (as well as any extracted heat from the process) to the energy introduced into the DFB gasifier and into the separation and upgrading section. The former corresponds mainly to the energy content of the fuel introduced. Energy can be introduced into the DFB, for instance in the form of electrical heating, in which case it also must be accounted for in the determination of the energy efficiency.



**Figure 2.** Conceptual description of a DFB process with emphasis on the carbon (indicated as “C”) and energy (referred to as “E”) efficiencies.

The carbon in the raw gas produced in the gasification reactor exists as numerous carbon-containing species. The carbon can be divided into two main categories: carbon in the form of products and carbon as  $\text{CO}_2$ , as shown in Figure 3. This distinction reflects the fact that within the DFB gasifier,  $\text{CO}_2$  constitutes the only carbon form from which no chemical energy, in the sense of heating value, can be extracted. The carbon in the products includes carbon in the forms of  $\text{CO}$ , light hydrocarbons (here defined as those with up to three carbon atoms), and heavier hydrocarbons (including tar). Therefore, three main forms of carbon are produced from the DFB considered in this work: carbon as part of the products; carbon as  $\text{CO}_2$  in the raw gas; and carbon as  $\text{CO}_2$  in the flue gases. An additional small carbon stream (not depicted in Figure 3) is the solid carbon from unconverted fuel particles that are entrained with the raw gas as fly ash; these are usually recirculated to recover the energy content of the carbon. Therefore, this carbon is recovered in either the combustor’s flue gas or the raw gas.



**Figure 3.** Conceptual representation of the flow of carbon through a DFB gasifier. The carbon flows that result from the fuel are shown in green, gold, and blue. The steam fed into the gasifier and the air fed into the combustor are also shown. The width of each carbon flow represents its approximate relative level in a typical DFB gasifier, and the widths of the steam and nitrogen flows represent the approximate amounts relative to the carbon flows. The red wavy arrows represent the energy input needed for separation of the streams.

In the raw gas from the gasifier, not all the carbon contained in the products is equally valuable. Depending on the intended output of the plant and the distribution of the product created by the fuel in the DFB process, some fractions may be valuable whereas others may have little value or are produced in too small quantities to justify being valorized or sold. Furthermore, some fractions, such as hydrocarbons with high boiling points, may incur operational issues downstream of the DFB section. The non-valuable carbon-containing species are often disposed of in the combustor, where their energy content contributes to fulfilling the heat demand of the gasifier and can, therefore, facilitate a higher level of recovery of carbon from the char in the raw gas. For instance, in the GoBiGas plant, tar is removed by a Rapeseed Methyl Ester (RME) scrubber and fed to the combustor, and BTX (Benzene, Toluene, and Xylene) are removed by active carbon beds and fed to the post-combustion chamber of the combustor [14].

The carbon in these non-valuable fractions can also be recovered as CO and light hydrocarbons by further cracking or reforming of the raw gas in a downstream reactor, for instance using Chemical-looping reforming [15]. However, the best option for converting the non-valuable carbon into valuable carbon is to manipulate the kinetics and thermodynamics of the reactions within the gasifier itself by adjusting the operating parameters or using catalytic materials, or by tuning the residence times of the fuel, gas, and bed material in the reactor [16]. Valuable carbon in the products can be converted to CO<sub>2</sub> in the raw gas by oxidation with oxygen or with steam, via the WGS reaction.

Depending on the extents of those reactions in the gasifier, a significant fraction of the carbon can be obtained in the form of CO<sub>2</sub>. In most cases, the upgrading and further synthesis of the product gas requires separation of the CO<sub>2</sub>, which means that this separation step is inherent to the cleaning sections of existing DFB gasification plants. Carbon from the CO<sub>2</sub> in the raw gas can, therefore, be recovered in a rather pure stream, which then becomes available for sequestration or for the synthesis of

hydrocarbons, for instance via the methanol-to-olefins route [17,18]. Nonetheless, as depicted in Figure 3, the separation of CO<sub>2</sub> from the raw gas entails an energy demand, for instance to desorb the CO<sub>2</sub> from its sorbent, the magnitude of which depends on the technology used. This increases the energy demand of the process and influences its overall energy efficiency.

Similarly, the separation of CO<sub>2</sub> from the flue gas strongly affects the energy efficiency of the DFB process. In a regular DFB process, the heat demand of the gasifier is fulfilled by burning part of the char with air, resulting in a CO<sub>2</sub> stream that is diluted with nitrogen, at a volumetric concentration of about 15%. This low concentration means that separation of the CO<sub>2</sub> from the flue gas is energetically demanding, making sequestration or further utilization of that carbon challenging, as it would greatly increase the plant's energy demand and decrease its energy efficiency. As mentioned above, the use of oxyfuel combustion resolves this energy penalty, although it introduces a new one in the form of production of pure oxygen, as illustrated in Figure 2.

In light of this discussion, three main ways to enhance carbon recovery in a DFB gasification process can be proposed. The first is to increase carbon recovery in the form of valuable products or as CO<sub>2</sub> by converting non-valuable hydrocarbons within the gasifier. The second is to produce a concentrated CO<sub>2</sub> stream in the combustor, one that is ideally ready for compression and sequestration, or for utilization, after minor purification steps. The third approach is to replace the heat source in the combustor with a carbon-free one, thereby allowing complete conversion of carbon in the gasifier. These three approaches are discussed in *Sections 1.2 to 1.4*.

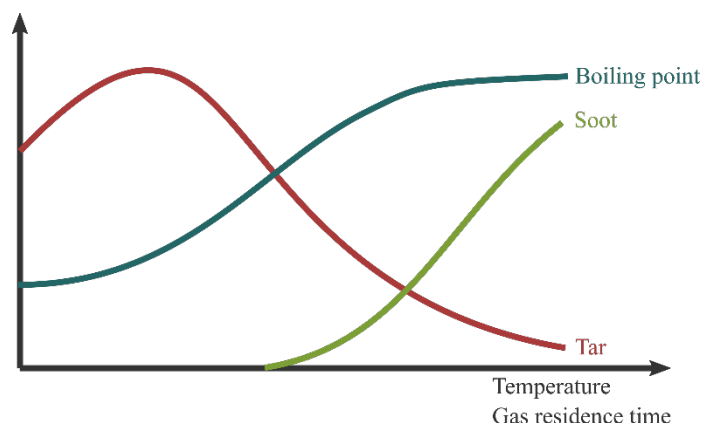
## 1.2. Increasing carbon recovery in the form of valuable products

As mentioned above, a strength of DFB gasification is its flexibility in adjusting the recovery of carbon in different forms. The carbon that is present in the products as non-valuable species can, to a certain extent, be transformed into valuable species within the gasifier, by adjusting various process parameters and bed material properties. The four main alternatives to steering the composition of the products towards enhancing the recovery of valuable compounds involve: (i) changing the temperature of the gasifier; (ii) using a catalytically active bed or modifying its catalytic activity; (iii) enhancing the extent of the gasification reaction; and (iv) decreasing the heat demand of the gasifier. These four possibilities are discussed in this section.

### 1.2.1. Temperature

The temperature influences the product distribution in the gasifier by affecting the reaction rates and the residence times of the gases. With an increase in temperature, the gasification reaction, as well as the cracking and reforming reactions intensify, overall resulting in the conversion of carbon to CO and light hydrocarbons. The composition of the tar is affected by the gasifier temperature. The tar is mainly monoaromatic and oxygenated at low temperatures and evolves towards non-oxygenated, unsubstituted polyaromatic hydrocarbons and benzene as the gasifier temperature is increased [19]. The yield of tar decreases with increasing temperature, as dealkylation and reforming reactions occur, but at some point, the cyclization of light hydrocarbons followed by polymerization results in the formation of soot. Moreover, the heavier polyaromatic hydrocarbons produced at higher temperature have high boiling points, which causes the dew-point of the raw gas to increase. The trends for the tar yield, boiling point, and yield of soot are illustrated in Figure 4. The increase in dew-point can result in fouling of heat recovery sections, creating severe operational issues. Moreover, a high gasifier temperature entails a high heat demand of the gasifier, which means that higher levels of carbon need

to be converted in the combustor to fulfill that heat demand, as compared with a lower temperature case. Therefore, a compromise must be found between, on the one hand, a low permanent gas quality and less mature tar, albeit with a lower heat demand and less troublesome tar, and, on the other hand, a high-quality permanent gas and high gasification rates, albeit with a higher heat demand and increased risk of operational issues.



**Figure 4.** Conceptual representation of the behaviors of the tar yield, its boiling point, and the soot yield with increases in process severity, i.e., involving increases in either or both the gasifier temperature and gas residence time.

### 1.2.2. Catalytic activity

The other main way to affect the carbon distribution in the products within the gasifier is to use a material that displays catalytic properties towards the reactions of interest. There are several ways to introduce catalytic activity into the gasifier. A material that has an intrinsic catalytic activity can be utilized as the bed material of the DFB process or mixed with an inert bed material. In a DFB gasifier that converts ash-containing fuels, an inert bed material can develop catalytic activity with time, due to the interaction of the fuel ash with the bed [20]. Besides, inorganic particles contained in or fed with the fuel, assuming that they are large enough to remain within the bed, can contribute to the catalytic activity of the bed. Ash species that are volatile can also have a homogeneous catalytic activity. Finally, additives can be used to enhance the catalytic activity. Note that additives that are introduced for other purposes can also contribute to the catalytic activity. For instance, limestone can be used to reduce  $\text{SO}_2$  emissions in the combustor [21] or to capture chlorine in the gasifier [22], and, under the conditions prevailing in DFB gasifiers, it is expected to form calcite, which is known to have catalytic properties that enhance tar abatement [23] and the WGS reaction [24]. The WGS reaction is generally desirable in gasification processes, as it increases the production of hydrogen and causes an increase in the  $\text{H}_2/\text{CO}$  ratio, which needs to attain a certain value set according to the downstream synthesis envisioned.

Catalysts that can be used in the DFB process are typically those used for steam reforming of a raw gas. The most widely used catalyst for this purpose is nickel [25], which is usually supported on alumina. Nickel catalysts are known to be highly effective at removing tar and increasing the yield of syngas [26]. Nonetheless, these catalysts are synthetic and, therefore, are expensive and suffer from rapid deactivation [27]. Moreover, Ni species are toxic [28], rendering the handling and disposal of Ni-based catalysts difficult. Other transition metals that are naturally available in large quantities and that are not toxic can be used as an alternative to nickel. For instance, iron ores have been shown to be active in tar reduction, as well as towards the WGS reaction [29,30]. Alkali and alkali-earth metals (AAEM) have also been extensively investigated as catalysts for biomass gasification. Minerals that

contain alkali-earth metal oxides, such as dolomites, calcites, and magnesites, are also known to have catalytic activities towards tar elimination [26,29] and the WGS reaction [26]. Alkalis are known to catalyze char gasification [31,32], the WGS reaction [33], and tar abatement [26,27].

The interaction of biomass ash, in particular AAEM, with bed particles has been shown to lead to catalytic activity, and is linked to the formation of ash layers on the particles [20]. The formation of these layers first requires interaction of the ash species with the particles, which can occur through condensation or a chemical reaction involving volatile ash species, such as alkali, the attachment of particles through van der Waals forces, or the sticking of molten ash particles [34–36]. The layers themselves are composed of several sublayers, formed as a result of the differences in diffusion rates of species within the particle crystalline structure and the replacement of atoms by those migrating ash species. Such mechanisms have been investigated for silica sand [37,38], olivine [39–41], feldspar [42–46], and bauxite [47], with respect to DFB gasification. In all these bed materials, the formation of the layers is characterized by the inner diffusion of Ca into the particles and its reaction with the crystalline structure, leading to the differentiation of the inner layer into two sublayers. The outer layer has a composition that resembles that of the biomass ash, i.e., for wood ash, it is predominantly Ca, Mg, and Si.

The ash layers formed by the interaction with biomass ash confer an improvement in gas quality and reduction of the tar content of the product gas *via* several mechanisms. Kuba *et al.* have shown that the catalytic activity towards light hydrocarbons (modeled by ethylene) and aromatics (modeled by toluene) is increased when the particles have an ash coating [48]. Moreover, the same authors have shown that the Ca-rich layers on used olivine increase its catalytic activity towards the reforming of 1H-indene, which is a stable intermediate in the decomposition of tar. The enhanced decomposition of 1H-indene has been shown to prevent its polymerization into polycyclic aromatics, such as chrysene [49]. In addition, Berdugo Vilches *et al.* have demonstrated that ash-coated olivine promotes the reforming of early tar precursors, thereby preventing their maturation to aromatic hydrocarbons [50].

While the catalytic activity of the ash layer is likely due to its high content of calcium (Ca), as suggested by Kuba *et al.* [48], the results presented by Berdugo Vilches *et al.* indicate that the interaction of the ash coating with the tar precursors also occurs in the gas phase [50]. This is supported by the suggestion that alkali is released from the bed in the gasifier [39,41]. Furthermore, Berdugo Vilches *et al.* have shown that potassium from a coated olivine, activated through K and S additions, is transferred to a char particle, mostly likely through the gas phase, which leads to an increase in the char reactivity [51]. Moreover, Knutsson *et al.* have shown that K can form mixed oxides with Ca in the ash layer of olivine particles, and they have proposed a mechanism through which this interaction leads to the surface becoming catalytically active for tar oxidation [52]. Consequently, both Ca and K play key roles in the development of catalytic activity through the formation of ash layers.

The buildup of an ash layer and the corresponding increase in catalytic activity of the bed, at least in the case of biomass ash, is an attractive feature of DFB gasifiers, since even if an inert bed is initially used, a very active bed can be obtained after a period of residence within the system. Through its catalytic activity, the ash layer contributes to converting carbon into a valuable and easy-to-handle form as CO and light hydrocarbons. However, it is worth considering the impact that this activity has on the WGS reaction. The ash layered-particles have indeed been shown to exhibit a higher catalytic activity towards the WGS reaction, as compared to their unlayered counterparts, in the cases of olivine and silica sand [48,49]. The WGS reaction is a key reaction because it is a follow-up to the tar and light hydrocarbons reforming reactions, as well as to the gasification reaction, and it converts carbon

to its final form in the gasifier, i.e.,  $\text{CO}_2$ . Consequently, as the catalytic activity increases, carbon is transferred from heavy hydrocarbons to light hydrocarbons, then to  $\text{CO}$ , and finally ending up as  $\text{CO}_2$ . Therefore, a balance needs to be achieved in terms of the recovery of carbon in valuable species and as  $\text{CO}_2$ , which places a limit on the desired activity level. Besides, as mentioned in *Section 1.1* and depicted in Figure 3, as carbon transfers to  $\text{CO}_2$ , the heat demand placed on the desorption step in the separation of  $\text{CO}_2$  increases.

### 1.2.3. Enhancing the gasification reaction

In order to increase carbon recovery in the gasification reactor and the disposal of non-valuable carbon compounds simultaneously, the char combustion can be partly replaced with the combustion of non-valuable species. This results in an increase in the rate of recovery of carbon as  $\text{CO}$  in the gasifier. However, it should be noted that for a given design of the DFB system, enhancing the degree of char gasification in the gasifier requires one or a combination of the following: (1) an increase in temperature; (2) an increase in the residence time of the char; and (3) the use of catalysts. All these solutions cause an increase in the heat demand of the gasifier, due to the endothermicity of the gasification reaction, which negates the desired effect. Furthermore, the use of a catalyst may result in the enhancement of the conversion reactions of the hydrocarbons that are meant for combustion. It is also worth noting that enhancing the gasification reaction does not increase the overall level of carbon recovery if the carbon in the flue gas is recovered.

The conversion of solid fuels in DFB gasifiers has been investigated in detail by Lundberg [53]. That author noted that fuel axial mixing significantly influences the char gasification rate. When pyrolysis occurred on the bed surface and char gasification took place in the deep bed, the char gasification rate was found to be up to 2-fold lower than in the alternative cases. The choice of bed material, in the sense of catalytic activity level, was found to affect greatly the kinetics of the gasification and its profile. The dominant fuel mixing regime was found to be strongly impacted by the gasifier's scale. At small scales, fuel dispersion dominates. As the scale increases, so does the residence time of the fuel. However, the fuel convection becomes the dominant mixing mechanism, since the bed material velocity increases with scale. This increase in bed material velocity also raises the likelihood that fuel particles pyrolyze on top of the bed, which leads to a less-reactive char pore structure and, thereby, a lower char gasification rate. Based on the obtained results, Lundberg [53] suggested that a combination of baffles, an active bed material, and appropriate operational conditions is likely needed to achieve the degree of fuel conversion required when gas production is the main target of the DFB gasification unit.

### 1.2.4. Decreasing the heat demand

Reducing the heat demand in the gasifier increases the amount of carbon available for conversion in the gasifier, mainly as char. There are various ways to decrease the heat demand that are not related to a change in the operating parameters of the DFB loop itself, i.e., that affect neither the temperature of the gasifier nor the circulation rate of the bed. This is particularly important given that the methods to increase carbon recovery mentioned in the previous sections will likely lead to an increase in heat demand.

One of the simplest ways to decrease the heat demand of the gasifier is to preheat the steam. Similarly, preheating the combustion air reduces the sensible heat losses, thereby increasing the temperature in the combustor. Drying the fuel also greatly reduces the heat demand of the gasifier. All these options can be implemented by taking advantage of heat integration, increasing the energy efficiency of the whole plant. If it is an option, changing the fuel to one that is richer in volatiles and that has a higher

oxygen content can reduce the heat demand. However, more volatiles lead to more heavy hydrocarbons, while a higher oxygen content will promote increased conversion of carbon to CO<sub>2</sub>. Decreasing the heat losses of both reactors contributes to enhancing carbon recovery in the form of valuable products. This can be achieved through improved insulation of the reactor and by refractory lining of the interior surfaces. Finally, using oxygen-enriched air in the combustor decreases the heat losses with the flue gas, which may increase the temperature in the combustor. This temperature increase is limited by the bed material and its interaction with the fuel ash, although it can be balanced through the recirculation of flue gases. Still, if the concentration of nitrogen becomes so low in the combustor that CO<sub>2</sub> separation becomes viable, full carbon recovery can be achieved.

### 1.3. Producing a concentrated CO<sub>2</sub> stream in the combustor

In order to facilitate CO<sub>2</sub> separation to the greatest extent possible, the air fed into the combustor can be entirely replaced with oxygen. Thus, a near-pure stream of CO<sub>2</sub> is obtained, only slightly diluted with oxygen and containing some impurities, such as SO<sub>2</sub> and NO<sub>2</sub>. Due to the absence of dilution with nitrogen, the dimensions of the combustor can be reduced and the amount of char required decreased, as explained above. The temperature in the combustor can be controlled by circulating the flue gases, which also allows for control of the bed circulation independently of the oxygen requirement.

Several technologies exist for the production of pure oxygen, the most widely applied being the cryogenic separation of oxygen from air in a so-called Air Separation Unit (ASU). Oxygen can also be produced by electrolysis of water, which has the advantage of also producing H<sub>2</sub>. H<sub>2</sub> can be used to adjust the H<sub>2</sub>/(CO+CO<sub>2</sub>) ratio of the syngas, for instance to obtain the optimal value for the methanolation process. Thus, full recovery of carbon as valuable species, such as syngas and olefins, could be achievable. It is worth noting that the electrolysis pathway can also serve as a way to balance the grid during periods of excess power production [17].

#### 1.3.1. Sorption-enhanced DFB gasification

The use of calcium oxide-containing bed materials in a DFB gasifier can lead to carbonation-calcination cycles, whereby CO<sub>2</sub> is captured by the bed in the gasifier and released in the combustor [54], under favorable conditions of temperature and CO<sub>2</sub> partial pressure in both reactors. This can be of interest when a high yield of H<sub>2</sub> is desired and oxy-combustion is carried out in the combustor. Indeed, the removal of CO<sub>2</sub> by the bed in the gasifier displaces the equilibrium of the WGS reaction, resulting in increased production of H<sub>2</sub> and CO<sub>2</sub>. This, in combination with the catalytic activity of calcium oxide species towards the reforming of tar and light hydrocarbons, allows for high H<sub>2</sub> yields. The combustor can be operated in oxyfuel mode, thereby enabling the recovery of CO<sub>2</sub>. This is of interest when negative emissions of CO<sub>2</sub> are desired, driving the use of biomass in combination with carbon capture. Nonetheless, the bed materials that are used tend to disintegrate and, for this reason, no commercial operation has been demonstrated in a DFB.

### 1.4. Carbon-free heat production in the combustor

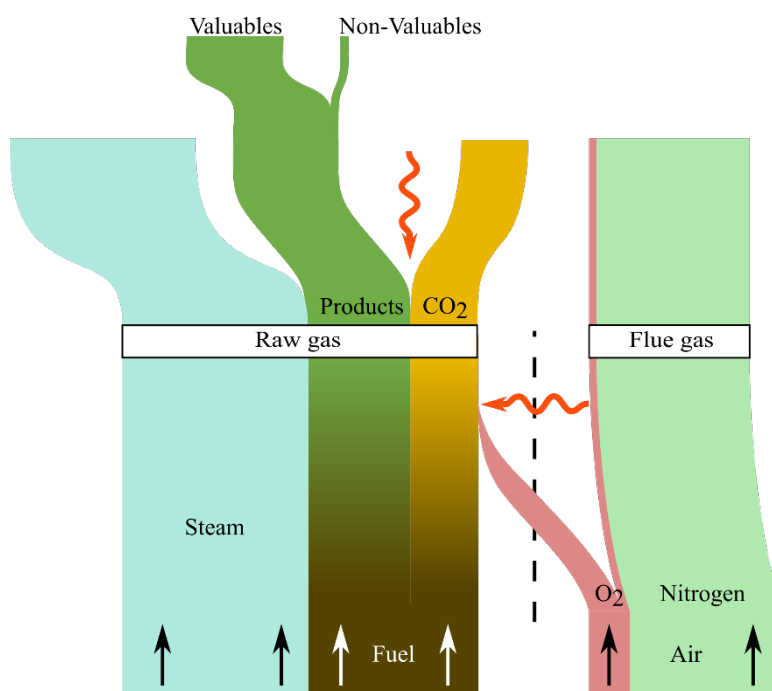
#### 1.4.1. Electrification

In theory, part or all of the heat demand of the gasifier can be covered by electrical heating. This can be achieved by placing electrical coils in a fluidized bed section prior to the combustor, so as to avoid erosion. Although it would be possible to heat the gasifier with coils directly, thus removing the need for a combustor, the products that are not valorized still need to be combusted. This includes the carbon in the gasification fly ash, which can represent a significant fraction of the total carbon. Furthermore,

the combustor is involved in regenerating the catalytic bed material. Consequently, the combustor is needed, and meeting all of the heat demand with electrical heating is not desirable. Electrical heating is likely to be feasible only if cheap and renewable electricity is available. Under these conditions, electrolysis may be affordable and more attractive than the use of an ASU, due to the product-polishing opportunity created by producing  $H_2$ . Electrical heating can also be used in a steam reformer downstream of the gasifier, to convert non-valuable, carbon-containing species into valuable ones.

### 1.4.2. Chemical-Looping Gasification

The concept of Chemical-Looping Gasification is based on the use of an oxygen carrier as the bed material in a DFB system [55]. When in contact with oxygen at high temperature, some materials, in particular metals, can be oxidized, thereby releasing an amount of heat comparable to the heat released by the combustion of char (per molecules of  $O_2$  consumed). In the reducing atmosphere of the gasifier, the oxygen can then be released, ideally by reacting with non-valuable species, or it may contribute to the gasification of the solid char. Since char is no longer needed to fulfill the heat demand of the gasifier, it can and should instead be gasified. This ideal case is depicted in Figure 5. Therefore, CLG offers the potential for full recovery of carbon on the gasifier side. Note that the reactor in which the oxidation occurs is usually called the “air reactor” (AR) and the gasifier is termed the “fuel reactor” (FR). These terms will be used in this thesis when discussing CLG, although they represent the same conceptual units as the combustor and the gasifier, respectively.



**Figure 5.** Conceptual representation of the flow of carbon through an ideal CLG unit. The carbon flows resulting from the fuel are shown in green and gold. The steam fed into the gasifier and the air fed into the combustor are also shown. The widths of the carbon flows represent their approximate relative amounts for an idealized CLG case, where the oxygen transport leads to an increase in the amounts of valuable products and a decrease in the levels of non-valorables, while the amount of  $CO_2$  is only slightly increased.

Despite the attractive features of the CLG process, there are a number of crucial obstacles that must be overcome for the process to reach the ideal scenario described in the preceding paragraph. Many of these issues are related to the oxygen carrier itself. Indeed, long-term operation of a CLG process requires the use of an oxygen carrier that remains stable under the thermal and mechanical stresses, as

well as under the stress created by the repeated reduction-oxidation cycles [56]. The material must also retain its reactivity long enough so that makeup feeding of fresh oxygen carrier is not required too frequently. Obviously, low-cost oxygen carriers are desirable, especially to alleviate the two aforementioned issues. In that aspect, using a waste or a waste-derived material as oxygen carrier would confer tremendous advantages. Finally, the heat of oxidation of the oxygen carrier must be sufficient to cover the heat demand of the gasifier under the conditions selected, and these conditions must be compatible with the thermodynamics of the reduction-oxidation of the material.

Another major challenge is to ensure complete conversion of the fuel in the FR. Obviously, complete conversion is not achievable given the stochastic nature of the mixing in the fluidized bed of the FR and the entrainment of fine carbon particles. Nonetheless, conversion is to be maximized, since any carbon lost to the AR is likely to be emitted to the atmosphere, given that the CO<sub>2</sub> concentration will be low, well below that of a regular DFB. One way to prevent char being transported to the AR is to use a so-called “carbon stripper”, as described elsewhere [57]. Note that the regeneration of the bed from potential coking also causes the emission of a small amount of carbon in the AR. However, the AR can no longer be used to combust non-valorized species, which must, therefore, be taken care of in another way.

Even if all these issues can be resolved, there remains the problem of the form in which carbon is recovered in the FR. Indeed, the oxygen transported to the gasifier is likely to react with the valuable carbon-containing species or with hydrogen, rather than with non-valuable species (generally tar). One reason for this is that the concentration of valuable (excluding CO<sub>2</sub>) carbon species is higher than that of non-valuables. Moreover, devolatilization is more likely to occur on the surface of the fluidized bed, due to the fuel particles being lifted by their own volatiles [58], and this is the position at which the gas-oxygen carrier contact is lowest. Finally, oxygen carriers react preferably with specific gas species, and react faster with H<sub>2</sub> and CO than with hydrocarbons, in particular the heavy ones. Consequently, a compromise must be found between the recovery of carbon in the FR in a valuable form and the “C-free” fulfillment of the heat demand in the AR.

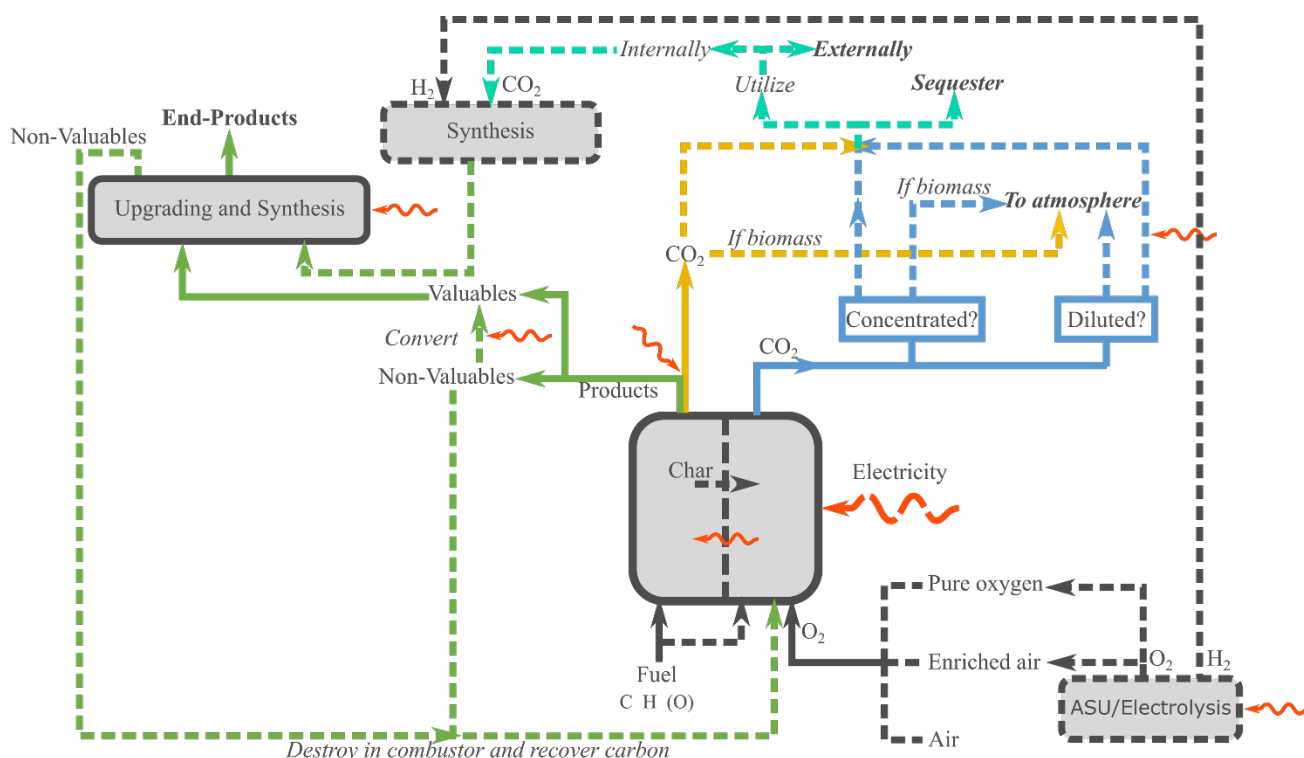
## 1.5. Carbon recovery as CO<sub>2</sub> exclusively: Chemical-Looping Combustion

If the circular use of plastics is well-established and sufficiently efficient to require only a limited input of biomass to compensate for the inevitable losses, then the manufacture of new chemicals or plastics from biomass is not justifiable. However, if removal of carbon dioxide from the atmosphere is attached a value by society, then the carbon in biomass will need to be recovered for sequestration. The use of oxygen carriers in a DFB system then becomes an attractive way of achieving this goal. By aiming for very high levels of oxygen transport between the reactors, the carbon from the biomass can be fully converted as CO<sub>2</sub> in a pure stream in the gasifier, while heat that is in excess to the FR’s heat demand is produced in the AR. This process, which is called Chemical-Looping Combustion (CLC), has been extensively investigated [55,56,59].

## 1.6. Summary of carbon recovery in DFB gasification systems

The possible routes for carbon recovery in a DFB gasification system are summarized in Figure 6. Ultimately, the carbon introduced into the DFB gasifier will end up: (1) as an end-product from the plant, including CO<sub>2</sub> for utilization outside the process; (2) being sequestered; or (3) being emitted to the environment. These three outcomes are bolded in the figure. As shown in Figure 3, three main categories of carbon are considered: carbon as a product, represented in green in Figure 3 and Figure

6; carbon as CO<sub>2</sub> in the raw gas, represented in gold; and carbon as CO<sub>2</sub> in the flue gas, represented in blue. The latter may be diluted or concentrated, provided pure oxygen is produced, either by an air separation unit or by water electrolysis. If the latter is used, the hydrogen byproduct can be reacted with CO<sub>2</sub> to recover its carbon in the upgrading and synthesis steps. CO<sub>2</sub> may also be emitted to the atmosphere, especially if its dilution level renders its separation extremely costly. However, in the contexts of the established circular economy and climate change issues, this emission is only acceptable if the carbon originates from biomass, since it then results in overall neutral emissions. Not shown in the figure is the carbon in the raw gas fly ash, which, as mentioned before, is generally burnt in the combustor. In addition, the fate of the CO<sub>2</sub> that is potentially formed during the upgrading and synthesis steps is not shown. This CO<sub>2</sub> will either be emitted to the atmosphere or be separated, after which it can be mixed with the other CO<sub>2</sub> streams.



**Figure 6.** Summary of the carbon pathways in a DFB gasification process, including the upgrading and synthesis section. Dashed arrows represent alternative pathways. Green arrows represent the carbon in products, gold arrows represent the carbon as CO<sub>2</sub> in the raw gas, blue arrows indicate the carbon in the form of CO<sub>2</sub> in the flue gas, cyan arrows indicate the mixed CO<sub>2</sub> streams, and wavy red arrows represent the energy input.

## 1.7. Aspects of carbon recovery in DFB processes investigated in this thesis

This thesis discusses three cases in which the aim is to increase carbon recovery in DFB gasifiers. The first case is based on the first approach discussed in the present chapter, i.e., increasing carbon recovery in the form of valuable species. To achieve this goal, a method to enhance the level of activity and activation rate of the bed material, based on the circulation of fly ash generated in the combustor of the DFB gasifier when converting biomass, is investigated.

The second and third cases are based on the CLG technology. The second case, described in **Paper A**, focuses on the issue related to producing a high-quality syngas during CLG of biomass and obtaining high fuel conversion rates in the FR. The oxygen carrier used in that case is waste from the steel-

making industry, namely LD-Slag. The third case, based on the work described in **Paper II**, focuses on achieving complete fuel conversion, when automotive shredder residue, a plastic waste, is converted in the DFB gasifier. The high metal ash content of this waste constitutes an intrinsic oxygen carrier, which may enable operation in the CLG mode. The feasibility of an actual CLG process that uses this waste as fuel and a source of oxygen carrier is investigated by examining the impacts of process parameters and by establishing the heat balance of the system.

The abovementioned three cases have in common that they provide value and exploit waste streams: as a catalytic additive in the first case, as an oxygen-carrying bed material in the second case, and as both a fuel and an oxygen carrier in the third case.

## Chapter 2: Possibilities for using waste in DFB gasification processes

Apart from its role as a carbon extraction process and its potential as a negative-emissions technology, DFB gasification could contribute to the circular economy by using waste. There are three main pathways through which the DFB gasification technology can utilize waste materials efficiently. The first way is to convert in the gasifier a carbon-containing waste rather than a fossil fuel or an energy crop. The second route is to replace the bed material with a waste to carry the same purpose: heat transport and thermal flywheel effect, and that has potential catalytic or oxygen-carrying effects. The third pathway uses waste as an additive to the process, so as to improve performance or drive the compositions of the products in a desired direction.

In this chapter, these three ways for DFB gasification to use waste are discussed in terms of the features of the wastes that make them suitable for use in the DFB and their expected behaviors in the system. For each pathway, the waste that was examined in the work of this thesis is presented and the investigations of its use in DFB gasification or similar applications are discussed. For the first two pathways, the considered waste is sourced externally from the process, whereas for the third pathway, the waste is sourced from within the process, thereby introducing an additional layer of circularity to the process.

### 2.1. Conversion of waste

An obvious possibility for waste utilization in DFB processes is the conversion of carbon-containing waste streams. As stated in the *Introduction*, these waste streams are either of biogenic origin, i.e., biomass waste, such as forest and agricultural residues or food waste, or of fossil origin, i.e., plastic waste (which can be contaminated with biogenic residues). Converting these wastes in DFB gasifiers entails several challenges, due to the nature of the wastes and the systems used to collect them. For instance, a plastic packaging waste stream contains many types of polymers, often contaminated with food and other biogenic residues, and it may contain contaminants from other waste-sorting streams, such as metals, glass, cardboard and paper. Although further sorting occurs after recycling by the consumer, some of those contaminants inevitably end up in the final plastic packaging waste.

To complicate matters further, plastic packaging rarely comprises only one type of polymer: multilayer packaging is common and combines many types of resins, as well as metal foils, coatings, and adhesives [5,60]. Moreover, plastics contain many additives that are used to enhance their properties, including antioxidants, photo-stabilizers, heat stabilizers, plasticizers, flame retardants, impact modifiers, compatibilizers, and dyes and pigments [6]. These additives can be organic compounds, such as phthalates used as plasticizers, or inorganic, such as calcium carbonate, which is used as a filler, or brominated compounds, used as flame retardants. Consequently, even a perfectly sorted, washed, and decontaminated plastic waste will still contain several types of polymers, as well as various inorganic compounds. In addition, the composition of plastic waste, for instance packaging waste, will vary from country to country and even locally, due to variations in collection schemes, sorting efficiency, and consumption patterns. A temporal variation is also expected, given that these systems evolve, as does the composition of a new plastic placed on the market by the industry.

This variability of composition of plastic waste streams means that it is challenging to predict the behavior of the waste in a conversion unit and the compositions of the products, making it difficult to fine-tune the process. In addition, given the potential inclusion of inorganic materials in the waste,

issues such as agglomeration, clogging, fouling, and corrosion render the operation of the process problematic. When converting biomass waste, the alkali content has to be carefully monitored, given that alkali interactions with silica from the bed material, dirt, and the mineral inclusions in the biomass itself, can lead to agglomeration [35]. Furthermore, the presence of halogens in the plastic waste means that, during conversion, persistent organic pollutants (POP) can be formed. These compounds include dioxins, polychlorinated dibenzofurans, and polychlorinated biphenyls. Care must be taken when converting waste that contains halogens to ensure that the emissions of these pollutants are minimized and below regulatory limits.

### 2.1.1. Impact of fuel composition on carbon recovery

The critical properties of the fuel with regard to the carbon distribution in a DFB system are its: (i) elemental organic composition, especially its C, H, and O contents; (ii) chemical structure; (iii) volatiles and fixed carbon yields; (iv) moisture content; and (v) ash content and the composition thereof. Fuels with a high concentration of oxygen will produce more CO and CO<sub>2</sub> than other fuels. This is the case for biomass compared with coal or plastic waste. These oxygen-rich fuels also tend to produce more oxygenated tar. The chemical structure of the fuel dictates the devolatilization step, as tar and light gas species are formed by decomposition of the carbon matrix. For example, the carbon backbone of polyolefins tends to undergo scission at random sites, whereas polymers with large side-groups, such as PMMA, tend to be depolymerized [61]. Note also that the chemical structure of the fuel determines whether a phase change occurs before devolatilization, which can have an impact on the heat demand of the gasifier. For instance, thermoplastic melting can act as a heat sink.

The yield of fixed carbon and volatiles from the fuel is itself dependent upon the chemical structure and composition of the fuel. It is also dependent upon the process conditions, i.e., heating rate, temperature, and pressure. Fuels with a high fixed carbon content produce a lot of char, and their carbon content is recovered as either CO (from gasification) or CO<sub>2</sub> (through oxidation in the combustor or the WGS reaction in the gasifier). Conversely, fuels with high levels of volatiles produce much more tar and generate lighter hydrocarbons from the tar decomposition. The fixed carbon level may be too low to be compatible with the regular, self-sustained operation of the DFB. Therefore, heat needs to be provided in another way, possibly by combusting non-valorized products or by combusting valuable products if the closure of the heat balance requires it. The combustion of an alternative waste fuel can also be carried out in the combustor.

The moisture content of the fuel has a significant impact on the heat demand of the gasifier, since the moisture acts as a heat sink. The increased heat demand leads to a necessary shift of carbon to CO<sub>2</sub> in the flue gases. The steam added to the system increases the degree of dilution of the reactive gases, thereby preventing, for example, the polymerization of aromatics. The ash content of the fuel can have a strong impact on the carbon conversion and, more generally, on the reactions within the gasifier. Indeed, reactive species may be present in the ash, acting as a catalyst or activator for the bed material. Conversely, these species can poison catalytic sites on a catalytic bed or react to form non-catalytic phases. From the energetic standpoint, if the ash content is high it acts as a heat sink, albeit not to the same extent as moisture does. Furthermore, ash that has an oxygen-carrying capacity, if it remains in the bed, allows for the displacement of carbon from the combustor to the gasifier.

### 2.1.2. Automotive Shredder Residue

In this thesis, a plastic-containing waste that is rich in metals was used as both the fuel and the source of the oxygen carrier for a CLG process. This waste, automotive shredder residue (ASR), is the remainder fraction of the shredding and sorting process for a car, corresponding to about 20%-25% of

the original weight of the vehicle [62]. After depollution and dismantling, shredding of the car body is carried out and the metals are separated, which results in a rest fraction that contains plastics, foams, non-ferrous inorganics, dirt, as well as metals that were not separated. This fraction, which is the ASR, is thus a highly heterogeneous carbon waste that contains high levels of inorganic compounds, notably metals [62–64]. Due to its metal content, ASR can be used to generate its own oxygen-carrying bed material for the CLG process, which is the subject of **Paper II**.

Based on these properties and regulatory pressures, there have been extensive investigations of ASR thermochemical recycling [62–65]. Indeed, EU Directive 2000/53/EC[66] requires the EU Member States to ensure that the reuse and recovery of end-of-life vehicles reaches a minimum of 95% (by average weight per vehicle per year), and that reuse and recycling should reach a minimum of 85%. Owing to the increasing use of lightweight materials, such as plastics and polymer composites, in car manufacturing [67], meeting these requirements will place intense pressure on the recycling of ASR. In addition to the external pressures, investigating the thermochemical recycling of ASR constitutes an interesting case study, as ASR is an example of the rest fraction that emerges from extensive sorting. The circular use of plastics means that homogeneous plastic streams with few impurities must be produced. The refuse from this process will typically consist of inorganics, probably including metals, as well as plastics due to process inefficiencies. As such, thermochemical recycling strategies that can be proven to be viable for ASR may be applicable to these wastes.

However, the lack of a standard definition or composition for ASR makes it challenging to find a technology that addresses the variability of its composition and its heterogeneity. Differences in shredding and separation process technologies and efficiencies, as well as the evolving composition of cars lead to differences at local and national levels. Furthermore, cars are rarely the sole input to shredders, which are typically also fed with scrap iron and white goods [63,65,68]. Nevertheless, ASR is expected to comprise polyolefins, polyurethanes, polyvinyl chloride, polyamides, polystyrene, and various blends of compounds, such as acrylonitrile butadiene styrene and glass fiber-reinforced polymers [64,69]. The metal fraction of ASR contains iron, aluminum, and copper in large amounts, as well as zinc, lead, chromium, and nickel [64,70]. It should be noted that the chlorine content of ASR can be high [63,70], which can lead to the formation of POP during thermochemical conversion [63,71].

## 2.2. Waste-derived bed materials

For a waste material to be suitable for use in a DFB gasification system, certain criteria must be met. The waste must be thermally and mechanically stable under the conditions of temperature and flow prevailing in the DFB loop. Materials with excessive attrition rates cannot be used, as the rate of makeup feeding of new bed material would be detrimental and the production of fines would be overwhelming. The melting point of the material must be well above the operating temperatures. If no further application exists for the material once it is no longer fit for use in the DFB, i.e., when it is extracted as bottom ash or fly ash, its disposal must then meet the environmental regulations in force.

The interactions of the bed with ash components released by the fuel in the gasifier must also be carefully considered. Particular attention must be paid to the risk of agglomeration, which is a consistent problem with alkali from biomass ash. Nonetheless, the waste material can develop a beneficial catalytic activity by interacting with the ash components. Conversely, the material could develop catalytic activity towards undesired reactions, or it could develop an oxygen-carrying propensity, which might be beneficial or detrimental depending on the aim of the process.

Waste-derived bed materials can be introduced into the DFB gasifier in the form of a waste fuel ash, provided that the ash content of that fuel and the sizes of the ash particles are sufficient to remain in the bed material loop and gradually replace the starting bed material. This type of intrinsic bed material is highly beneficial in terms of the cost-competitiveness of the process, since the cost associated with makeup feeding of bed material is avoided. ASR is one example of a type of waste fuel that provides its own bed material. Due to the high metal content of the ASR ash, as mentioned in *Section 2.1.2*, catalytic and oxygen-carrying properties can be expected to develop when the ASR-ash bed is formed. However, it should be pointed out that therein also lies a crucial issue with bed materials derived from ash-rich waste fuel: if the ash forms a bed with undesirable properties, then the cost associated with maintaining a bed with the desired properties becomes high.

### 2.2.1. LD slag: a metallurgic waste

A metallurgic waste, LD slag, was investigated for its potential as an oxygen-carrying bed material for CLG. LD slag, which is also known as steel converter slag or Basic Oxygen Furnace slag, is a byproduct of the steelmaking process, more specifically of the basic oxygen steel production process, also known as the Linz-Donawitz process, from where it takes its name. In general, LD slag is produced in large quantities, at 85–165 kg for every tonne of steel produced [72]. The elemental composition of LD slag (on an oxides basis) is dominated by CaO (30%–60%), FeO (5%–38%), and SiO<sub>2</sub> (8%–26%), and it can contain significant amounts of MgO, MnO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, and V<sub>2</sub>O<sub>3</sub> [72–75].

LD slag is not a hazardous waste and is suitable for use in a wide range of applications. For instance, it can be used as a soil stabilizer and conditioner, as fertilizer, for road-making, or for CO<sub>2</sub> capture and flue gas desulfurization [75,76]. Given its iron content, LD slag shows potential for use in chemical-looping applications, such as CLC and CLG, as well as in chemical-looping reforming, which is a technology that upgrades a raw gasification gas by converting tar. The potential of LD slag in these applications has mostly been investigated at the laboratory scale. Its ability to convert hydrocarbons, modeled by CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, has been shown to be poor [77,78], especially with respect to CH<sub>4</sub>, although it has displayed reactivity and CO<sub>2</sub> yield comparable to those of ilmenite when converting syngas [79].

LD slag has also recently been investigated at the semi-industrial scale, as an oxygen carrier for Oxygen-Carrier-Aided Combustion (OCAC), which is a CFB combustion process that takes advantage of the properties of oxygen carriers to improve the performance of the process and reduce emissions [80], notably of CO. Rydén *et al.* have shown that, when mixed with silica sand, LD slag generates decreased CO emissions, although it did not perform as well as other oxygen carriers, such as ilmenite when investigated in the same CFB [81]. When only LD slag was used as the bed material, the CO emissions increased compared with silica sand, which is attributed to the limited capability of the material to absorb ash components, in particular K.

The changes that occur in the physical and chemical properties of LD slag due to its use as an oxygen carrier for OCAC in the aforementioned experiments were studied in a batch reactor by Hildor *et al.* [82]. They found that the reactivity of the material towards syngas, CH<sub>4</sub> and benzene conversion decreased slightly with the time spent in the CFB system. The oxygen-carrying ability of LD slag was attributed to the reduction of magnetite to wüstite, with both crystal structures including dopants, such as Mg and Mn. The oxide phases were found to be independent of the operational time in the CFB or in the batch-scale reactor. Fuel ash elements were found in the bed material, with K being found at low levels in the Si- and Al-rich areas.

As pointed out by Hildor *et al.*, LD slag has a relatively poor oxygen-carrying capability, which may make it more suitable for OCAC and CLG processes than for CLC [82]. Furthermore, the limited

absorption of alkali by the material, which may be problematic in CLC and OCAC, is not as detrimental in CLG and can actually be beneficial, as it may result in an increased partial pressure of alkali and, thereby, increase homogeneous catalysis.

## 2.3. Waste as additive

The use of additives in DFB gasification can serve multiple purposes. Limestone is frequently used in CFB boilers for desulfation and can serve the same purpose in a DFB system. In addition, it can capture chloride, so as to avoid HCl or POP emissions. Catalytic particles could be added to the bed material to increase its activity. Additives can also be added to enhance the properties of the bed material. For instance, K-salts were added during the start-up of the GoBiGas DFB plant, to increase activation of the bed [10]. Waste that is sourced externally from the process may be used as an additive if it has the desired sorbent, catalytic, or activity-inducing properties, provided that its use does not introduce harmful components. In this thesis, a waste produced by the process itself, namely the fly ash, was considered as an additive in DFB gasification.

### 2.3.1. Waste inherent to the DFB process: fly ash circulation

The main wastes produced by the DFB process are: the bottom ash, which is extracted from the bottom of the combustor bed; and the fly ash, derived from the gasifier raw gas and the combustor flue gas. The first stream contains mainly larger bed material particles, agglomerates, and impurities present in the fuel, such as sand or nails. The second stream comprises mainly attrition-derived bed particles, small fuel ash particles, and aerosols that are formed from condensing ash components.

The bottom ashes of DFB gasifier are expected to resemble those obtained from CFB combustion of the same fuel. They can, therefore, be expected to be used in similar applications, typically in cement and concrete production [83]. The available routes for the utilization of gasification fly ash are fewer, due mainly to its high carbon content, polyaromatic hydrocarbons, and, in the case of waste gasification, high contents of chlorine and heavy metals [83–86]. A few options exist for direct utilization, e.g., as an alternative fuel, for instance in cement kilns, as a filler in asphalt and asphalt-like products, or as a component of lightweight aggregates. Pretreatment of the fly ash expands the range of options, in particular washing to remove chloride and alkali, heat treatment to decrease the carbon content, and leaching of heavy metals. After treatment, gasification fly ashes could be used in construction, as fillers in concrete mortar, as road base, and as fertilizer or soil stabilizer, among other options [83–86].

Although finding uses for the ashes generated from DFB gasification is crucial, possibilities to take advantage of these ashes within the system should be investigated. In the GoBiGas DFB plant, the product gas ash from the gasifier, containing 10%–15%wt of carbon, is circulated back to the combustor for carbon and energy recovery [10], while the coarse flue gas ash is circulated back to the gasifier, mainly to increase bed material retention in the loop. However, this external material loop (in addition to the internal loop involved in bed material circulation) also reintroduces ash components and potential additives to the system, which will have impacts on the performance and operation of the process.

These ash loops are associated with some negative consequences, as discussed by Kirnbauer *et al.*, who studied the balance of inorganics in the DFB system of the Güssing plant [8]. These authors reported that the ash loops caused significant accumulations of low-melting-point substances in the system. The accumulation of K was identified as being particularly critical, due to its roles in fouling, slagging, and bed agglomeration. They recommended that the recirculation of fine fly ash from the

combustor should be avoided. However, the potential beneficial effects of the accumulation of such active species as K were not investigated.

At the intersection between the use of waste as a bed material and as an additive, Kuba *et al.* have investigated the impact of replacing part of the makeup of fresh material, in that case olivine, with ash-layered olivine recovered from the bottom ash of the combustor [9]. This replacement was carried out as part of the optimization of the organic flows in the HGA Senden DFB gasifier, wherein the fuel is logging residues, which contain large quantities of foreign mineral matter, mostly quartz. The bottom ash was sieved to remove the large quartz particles, and the active, layered olivine particles were collected and fed back into the DFB loop. This new ash loop replaced the circulation of coarse flue gas ash, which was instead discharged. The authors reported improved performance of the gasification process as the hydrogen concentration increased, whereas the level of methane decreased, and the concentrations of tar components, most significantly naphthalene and acenaphthylene, also decreased.

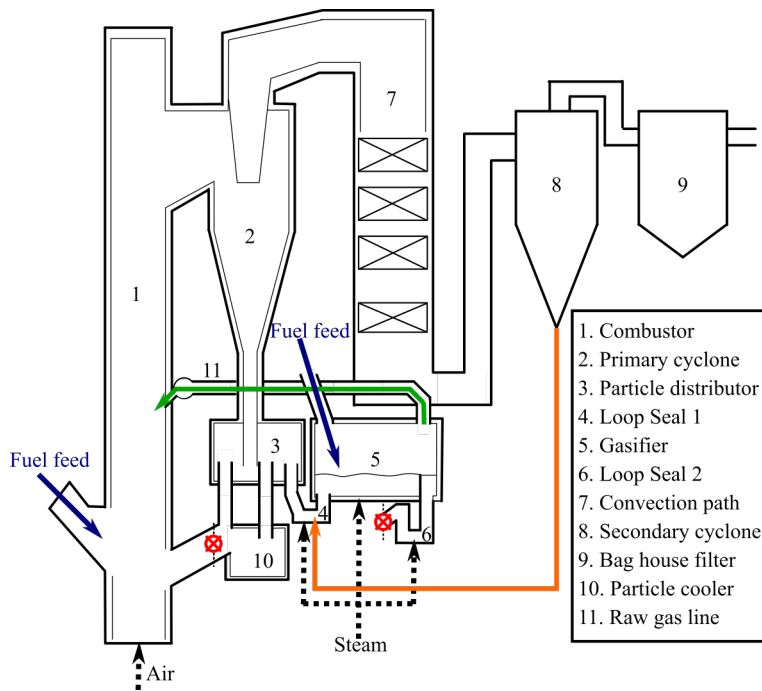
# Chapter 3: The Chalmers Dual Fluidized Bed Gasifier

The gasification experiments described in this thesis were carried out in the Chalmers DFB gasifier. In this chapter, this gasification facility is described, as well as the raw gas sampling and analysis equipment. The determinations of the carbon and energy balances of the gasification reactor are explained. Finally, the compositions of the bed materials and fuels used in the various experiments that constitute this thesis are reported.

## 3.1. Description of the unit

The Chalmers DFB gasifier consists of a 12-MWth circulating fluidized bed boiler, to which a 2–4-MWth bubbling bed gasifier has been retrofitted. The boiler is fed wood chips and wood pellets. The boiler is designed to provide heat to the Chalmers University campus over the winter. As a consequence, it is over-dimensioned when one considers a combustor that would operate with the 2–4-MWth gasifier if the DFB was operated as a standalone unit. Being a research facility, the Chalmers DFB gasifier is not equipped with a raw gas cleaning or upgrading section. Instead, the raw gas is fed to the boiler. Note that this means that one half of the external material loop described in *Section 2.3.1*, namely the circulation of gasification fly ash, is permanently implemented in the Chalmers' gasifier. Hereinafter, the CFB boiler is referred to as the 'combustor'.

A schematic of the Chalmers DFB gasification unit is shown in Figure 7. The circulating fluidized bed combustor is comprised of the combustor itself (#1 in the figure) and the primary cyclone (#2), which when the unit is operated in CFB mode only, returns the bed to the combustor *via* the particle distributor (#3). Located between the particle distributor and the return leg of the combustor is a particle cooler (#10), the purpose of which is to extract additional heat, if needed. Heat from the flue gases exiting the combustor is recovered in the convection path (#7), and the particles contained in the flue gas ashes are collected by a secondary cyclone (#8). Finer particles that are not captured by the secondary cyclone are trapped in a bag house filter (#9). When the unit is operated in DFB mode, the bed material circulates from the particle distributor to the gasifier (#5) *via* the first loop seal (#4). The bed material returns to the combustor through a second loop seal (#6), which is connected to the return leg of the combustor. This connection is represented by the two red dots in the figure. The positions of the fuel feed-points to both the combustor and gasifier are indicated by blue arrows. The combustor is fluidized with air, whereas the gasifier is fluidized with steam, although it can be fluidized with flue gases when no fuel is fed into it. For an extensive description of the unit, the reader is directed to the work of Larsson *et al* [87].



**Figure 7.** Schematic of the Chalmers' DFB gasifier. The blue arrows represent the positions of the fuel-feeding to the combustor and the gasifier, respectively. The green arrow represents the raw gas line, underlining that it is fed to the combustor. The orange arrow represents the circulation of the coarse flue gas ash that is collected from the secondary cyclone (#8) to the gasifier via the first loop seal (#4). This was part of the investigation carried out in **Paper I**. The red symbols in the figure are in reality physical connections, whereby loop seal 2 (#6) feeds into the return leg to the combustor.

As mentioned above, the raw gas line (#11) feeds directly into the combustor, as indicated in Figure 7 by a green arrow. This arrow also represents the circulation of the gasifier fly ash. The second half of the external material loop, in this case the circulation of coarse flue gas ash, is represented by an orange arrow. The coarse flue gas ash collected from the secondary cyclone can be fed to the loop seal 1 (#4 in Figure 7), thereby completing the external material loop. The consequences of the coarse flue gas ash circulation for the gasification process were investigated in **Paper I** and will be discussed in Chapter 4.

It should be emphasized that gasification measurements are only possible when the manpower is available for both the CFB side and the gasifier side. The CFB is operated continuously but manned for only two six-hours shifts each day. During the remainder of the time, fuel is not fed into the gasifier, which is then fluidized with flue gases. This means that on the CFB side, the fuel input is constant, and is about an order of magnitude higher (in terms of mass flow) than the fuel input to the gasifier, which is intermittent. This has a significant impact when one considers the roles of ash flows and ash accumulation. When feeding biomass to the gasifier it has to be kept in mind that the ash input is in that instance dominated by the CFB side. When feeding ash-rich waste, such as the ASR described in *Section 2.1.2*, one must consider that the biomass ash input from the CFB side is not negligible.

### 3.2. Raw gas sampling and analysis

The raw gas produced by the gasifier is characterized by extracting a slipstream from the raw gas line and then cleansing it of particulate matter in a high-temperature filter. From there, the slipstream is separated into two sub-streams for further analysis. The first sub-stream is used to sample the tar and

determine the dry gas composition, while the second sub-stream is passed through a high-temperature reactor (HTR) to determine the total carbon content of the raw gas.

From the analyses of the two sub-streams, only the concentrations of permanent gas species and SPA-tar become known. To determine the yields and establish the carbon balance of the system, a tracer, helium (He) gas, is introduced into the gasifier with the fluidizing steam at a known volumetric flow. The He balance across the system can then be used to convert the concentrations into product yields, expressing their quantities in moles or mass of product per unit mass of dry, ash-free fuel fed (referred to as 'daf').

The first sub-stream is quenched with cold isopropanol, to remove condensable hydrocarbons and steam. Once dry, the stream is led to a micro-GC Varian CP4900 equipped with a PoraPLOT Q and an MS 5Å column, using He and Ar as carrier gases. The GC measures the concentrations of H<sub>2</sub>, He, N<sub>2</sub>, CO, O<sub>2</sub>, 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>6</sub>, C<sub>3</sub>H<sub>8</sub>, and H<sub>2</sub>S. Thus, the permanent gas composition is determined. Prior to quenching, a port allows sampling of the tar by the solid-phase adsorption (SPA) method. In this method, the gas is passed through an adsorbent column that contains a first layer of 500 mg of aminopropyl-bonded silica, and a second layer that contains 500 mg of activated carbon, the purpose of which is to capture benzene, toluene, and xylene (BTX), which are not adequately absorbed by the first layer. The adsorbed tars are eluted from the columns and are thereafter analyzed in a BRUKER-430 GC equipped with a flame ionization detector. The heavy hydrocarbons with boiling points ranging from those of benzene to chrysene are thus quantified. The hydrocarbons that have boiling points within this range are defined as 'tar' in this thesis. The SPA method and its application for measuring the tar from the Chalmers' gasifier have been described previously by Israelsson *et al* [88].

The second sub-stream is reacted at 1700°C in the HTR, thereby cracking the hydrocarbons and gasifying the soot to form exclusively H<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O. The gas is filtered to remove any remaining soot particles, then steam is condensed, and the dry gas is led to a second micro-GC (of the same model as that used for the first slipstream line), equipped with PoraPLOT U and MS 5Å columns, and using He and Ar, respectively, as carrier gases. The HTR and its use in determining the total carbon from the raw gas have been described by Israelsson *et al* [89].

The measurements reported in this work correspond to periods of more than 20 minutes during which the temperature, fuel feeding rate, steam flow, and circulation rate can be considered as stable. Chromatograms are taken every 3 minutes, and the gas concentration for the measurement point is the average of the results from those chromatograms. Similarly, the tar concentration is the average of the concentrations obtained from the SPA samples, which, in general, are collected in the number of at least four.

### 3.3. Carbon balance

The total carbon determined in the HTR is used to assess the carbon distribution in the various outputs of the gasifier. The degree of conversion or, alternatively, the amount of carbon in the unconverted fuel leaving the gasifier is assessed by comparing the total carbon from the HTR to the carbon content of the fuel. Note that this includes the char and non-devolatilized fractions of the fuel that circulate to the combustor with the bed, coking onto the bed particles, as well as the small carbon particles and soot that leave with the fly ash. The amount of carbon contained in all the hydrocarbons with at least four carbon atoms, referred to as *total organic compounds* (TOC) in this work, is assessed by comparing the total carbon from the HTR to the carbon in the permanent gas. Among the TOC, those

species that are outside the SPA measurement range, referred to as *undetected condensable species* (UCS), are assessed by comparing the total carbon to the sum of the permanent gas and SPA-tar carbon.

The oxygen transported into the gasifier by the bed material is also determined using the HTR, by establishing the oxygen balance over the gasifier, as described by Israelsson *et al* [89]. Equation 1 shows the calculation of the oxygen transport, where  $n_i$  refers to the yield of C, H, and O, the subscript *fuel* indicates the yield of CHO in the fuel, *HTR* indicates the yield of CHO measured in the gas downstream of the HTR, and *tr* refers to the transported oxygen.

$$n_{O,tr} = (n_{O,HTR} - n_{O,fuel}) - (n_{C,HTR} - n_{C,fuel}) \cdot \left[ \frac{O}{C} \right]_{unc} - \left( n_{H,HTR} - n_{H,fuel} - (n_{C,HTR} - n_{C,fuel}) \cdot \left[ \frac{H}{C} \right]_{unc} \right) \cdot \left[ \frac{O}{H} \right]_{H_2O} \quad (1)$$

The oxygen transport is calculated as the difference between the oxygen measured in the HTR and the oxygen contained in the fuel, i.e., the first term of the equation. The oxygen contained in the char leaving the gasifier must be removed from this difference, which corresponds to the second term of the equation. However, oxygen addition also occurs in both the gasifier and the HTR through reaction of the gases and the fuel particles with steam, *via* the gasification reactions, the steam reforming reactions, and the WGS reaction. As every mole of oxygen reacted from the steam corresponds to two moles of hydrogen added to the gas, it is possible to remove that contribution to the oxygen balance. This corresponds to the third term of the equation. In the latter term, the hydrogen leaving the gasifier as unconverted fuel is also removed from the difference in hydrogen between the HTR and the fuel.

The accuracy of the total carbon determination in the HTR is dependent upon the HTR operating as intended, meaning that no carbon from the raw gas is unaccounted for in the calculation. If some carbon is missed, then the carbon in the unconverted fuel is underestimated, and so is the carbon in the TOC and UCS. The HTR was designed to operate at a temperature and residence time that maximize soot gasification. While the temperature is not expected to vary, fluctuations in the DFB system can lead to insufficient concentrations of steam with regard to the amount of carbon or too-long residence times. This can happen when fluctuations cause sudden low rates of steam flow and high fuel feeding rates. This issue is particularly prone to arise with low-oxygen-content fuels, such as plastic waste. Operations conducted at high fuel flow and low steam flow rates magnify the risk of fluctuations.

It is possible to assess how much carbon has been missed over an entire day and, from this, deduce an average value for the fraction of carbon from the fuel that is missed in the total carbon measurement over that specific day. This is achieved by passing air through the HTR and its filter, thereby inducing combustion of the soot that could not be converted in the HTR. In the case of conversion of ASR in the Chalmers' gasifier, the underestimation of the carbon balance was estimated to be, on average, between 0.6% and 2.6% of the carbon in the fuel. When wood pellets are used as the fuel, the error on the carbon balance is usually below 1%. This method has some obvious limitations. For example, over a day, various operating parameters are usually investigated, which are more or less prone to conditions that lead to insufficient soot gasification in the HTR. Nonetheless, this method gives a valuable estimation of the degree of error for the total carbon balance.

### 3.4. Energy balance

The energy or heat balance of a theoretical DFB system with a gasification reactor such as the Chalmers' gasifier can be assessed by determining the heat demand of the gasifier and the heat output of a theoretical combustor that would burn the unconverted fuel from the Chalmers' gasifier. When determining the energy balance of the theoretical CLG system, the method applied is the same but the heat of oxidation of the bed becomes prevalent. Given the complexity of the reactions taking place

within the gasifier, the heat demand is not determined as the sum of the sensible heat and heat of reaction within the reactor but rather by the difference in energy content between the outgoing and ingoing streams. This approach is similar to that used by Alamia *et al* to establish the heat balance of the GoBiGas plant [14,90]. The main assumptions on which the heat balance is based are described in **Paper II** and in its *Supporting Information*. Note that the theoretical combustor (or AR for CLG) is assumed to operate at a temperature 50°C higher than the gasifier, with an excess air ratio of 1.2 with regard to the oxidation of both the unconverted fuel from the gasifier and the bed material, and its heat loss is assumed to be recovered in the form of air preheating.

When oxygen carriers or bed materials that develop an oxygen-carrying capacity are used in the DFB system, the heat of oxidation of the bed material is of the same magnitude as the heat of combustion of the unconverted fuel from the gasifier. It is, therefore, crucial to be able to derive a reasonable range for this heat of oxidation. In the case of bed material formed from a complex mixture of metals, this may prove to be challenging. The bed material in **Paper II** exemplifies this case, as not only is the ASR-ash itself a complex mixture of metals, but also the bed contains a large fraction of olivine, which may itself have developed an oxygen-carrying capacity during the formation of an ash layer. Indeed, the ash layer of olivine, formed by interactions with biomass ash, is rich in Ca, which could lead to Ca sulfides-sulfates cycles between the two reactors, resulting in the transport of oxygen from the combustor to the gasifier. The thought process followed to estimate the value of the heat of oxidation of that complex mixture is described in **Paper II**.

The heat demand of the gasifier, HD, and the heat output of the combustor, HO, are determined as shown in Eqs. (2) and (3), respectively. All the terms of the heat balance are expressed in MJ/kg daf. Sensible heat terms are represented by  $\Delta H$ , and the terms related to chemical energy, i.e., lower heating values and heat of oxidation of the bed, are represented by  $E$ .

$$HD = (\Delta H_{pg} + \Delta H_{toc} + \Delta H_{unc} + \Delta H_{ash,G} + E_{pg} + E_{toc} + E_{unc}) - (\Delta H_{fuel} + \Delta H_{purge} + \Delta H_{steam,G} + (-E_{oxi}) + E_{fuel}) \quad (2)$$

$$HO = (\Delta H_{unc} + \Delta H_{ash,G} + \Delta H_{steam,C} + \Delta H_{air} + E_{unc}) - (\Delta H_{fg} + \Delta H_{ash,C} + (-E_{oxi})) \quad (3)$$

The subscripts used in these two equations have the following meanings:

- *pg* refers to the product gas, including steam;
- *toc* refers to the total organic compounds;
- *unc* refers to the unconverted fuel;
- *ash,G* and *ash,C* refer to the ashes at the temperatures of the FR and AR, respectively;
- *steam,G* and *steam,C* refer to the steams entering the FR and AR, respectively;
- *fuel* refers to the fuel, including moisture and ash, fed to the FR;
- *pur* refers to the purge gas introduced with the fuel feeding system;
- *fg* refers to the flue gases from the AR;
- *air* refers to the air fed to the AR; and
- *oxi* refers to the oxidation of the bed material.

Notice the sign of the heat released by oxidation of the bed material,  $E_{oxi}$ . This convention is chosen because the oxygen carrier is at a higher energy level in its reduced form than in its oxidized form. The reduced form of the oxygen carrier is arbitrarily attributed an energy level of zero, and its oxidized form is assigned an energy level corresponding to the heat of oxidation of the bed, i.e.,  $(-E_{oxi})$ . Therefore, the change in energy level across the combustor is  $(-E_{oxi})$  and the change across the FR is  $(+E_{oxi})$ , which correspond to exothermic and endothermic reactions, respectively. Note that the reaction

of the oxidized oxygen carrier with the gas species in the FR can be either endothermic or exothermic [91].

## 3.5. Materials

### 3.5.1. Bed materials

Various bed materials have been used in the work presented in this thesis. With time spent in the DFB system, these materials evolved by interacting with ash components. This entailed structural changes caused by a succession of reductive-oxidative cycles and high temperatures, and changes brought about by thermal and mechanical stresses. Furthermore, in Chapters 4 and 5, general trends combining the results from many different experiments across several experimental campaigns are presented. It is, therefore, unreasonable to detail the composition of each and every bed material at every stage of its evolution. Consequently, the compositions of only a few bed materials are shown in this section.

The results from **Paper I** that are discussed in this thesis relate to the use of coarse flue gas ash as an additive to increase the activity of the process and, thereby, the rate of carbon recovery in the form of valuable products. As will be discussed in further detail in Chapter 4, the production of sufficient coarse flue gas ash to enable its recirculation into the DFB system required the stimulation of its production, *via* the injection of olivine fines. The composition of these olivine fines, as well as the starting composition of the olivine used as bed material in that work, are described in the **Paper I** columns of Table 1. Note that the experiments discussed in **Paper I** follow involve measurements taken after the addition of  $\text{CaCO}_3$  and  $\text{K}_2\text{CO}_3$ , as well as two days of exposure to biomass ash, so the actual starting bed composition differs from that shown in Table 1.

**Table 1.** Elemental compositions of the main bed materials investigated in this work. Values are shown in %wt.

| Element | Paper I |               | Paper II |             | Paper A     |          |           |         |         |
|---------|---------|---------------|----------|-------------|-------------|----------|-----------|---------|---------|
|         | Olivine | Olivine fines | Olivine  | ASR-ash bed | Silica sand | Ilmenite | Manganese | Olivine | LD slag |
| Al      | 0.24    | 0.17          | 0.14     | 1.60        | 0.09        | 0.19     | 3.40      | 0.13    | 0.64    |
| Si      | 19.49   | 19.54         | 19.00    | 18.00       | 46.36       | 0.19     | 3.72      | 19.00   | 5.56    |
| Fe      | 5.18    | 5.32          | 4.90     | 7.70        | 0.04        | 24.48    | 5.15      | 4.70    | 18.61   |
| Ti      |         |               |          | 0.35        |             | 30.57    | 0.23      |         | 0.78    |
| Mn      |         |               | 0.34     | 0.46        |             | 0.82     | 37.73     | 0.29    | 2.09    |
| Mg      | 29.91   | 29.43         | 29.00    | 18.00       |             | 0.60     | 0.25      | 29.00   | 5.49    |
| Ca      |         |               | 4.50     | 7.10        |             | 0.01     | 1.88      | 3.40    | 28.44   |
| Ba      |         |               |          | 0.30        |             |          |           |         |         |
| Na      |         |               | 0.23     | 0.59        |             |          |           | 0.16    |         |
| K       |         |               | 1.50     | 1.70        |             |          | 0.99      | 1.10    |         |
| P       |         |               | 0.30     | 0.72        |             |          |           | 0.20    |         |
| Cl      |         |               |          |             |             |          |           |         |         |
| Br      |         |               |          |             |             |          |           |         |         |
| S       |         |               | 0.13     | 0.18        |             |          |           | 0.13    |         |
| Cr      | 0.21    | 0.45          | 0.03     | 0.07        |             |          |           | 0.04    |         |
| Ni      | 0.25    | 0.25          | 0.22     | 0.16        |             |          |           | 0.05    |         |
| Zn      |         |               | 0.07     | 1.40        |             |          |           | 0.05    |         |

The elemental compositions of the bed materials investigated in **Paper II** and **Paper A** are also shown in Table 1. The experimental campaign on which **Paper II** was based began with an olivine bed material that had substantially interacted with biomass ashes, as evidenced by its high Ca and K contents. The part of that campaign on which the investigation of the CLG of ASR was based took place on Days 9–13 of the 13-day experimental campaign. Concerning **Paper A**, LD slag was evaluated as a waste-derived oxygen carrier for CLG and was compared with two other oxygen carriers that have been extensively investigated for CLC and OCAC, namely an ilmenite and a manganese ore. In addition, as explained further in *Section 5.1*, the performances of the oxygen carriers were compared with two reference materials: silica sand, which is an inert bed material; and an extremely active olivine. The compositions of the three oxygen carriers and the two reference materials are listed in the **Paper A** column of Table 1.

### 3.5.2. Fuels

The situations regarding the fuels used in the studies of this thesis are similar to those for the bed materials. Many different batches of wood pellets were fed to the gasifier and wood chips were fed to the boiler across all the experiments reported in this work. Nonetheless, there was little variability in the compositions of those fuels, aside from the moisture level, which was most variable for the wood chips and did not affect the operation of the gasifier. For this reason, the proximate compositions of the wood chips and wood pellets in **Paper I**, as reported in Table 2, are assumed to be representative of all cases in which wood pellets were used in the gasifier. The average composition of the wood pellets from the experiments discussed in **Paper A**, based on four different experimental campaigns, is also shown, to highlight the similarities in composition. Finally, the proximate analyses of the two batches of ASR used in **Paper II** are shown in Table 2. Note that these batches are numbered 2 and 3 because a first ASR batch was used in the first days of the experimental campaign, prior to the measurements of interest.

**Table 2.** Proximate analysis of the fuels used in this thesis.

|                                              | <b>Paper I</b> |              | <b>Paper II</b> |             | <b>Paper A</b> |
|----------------------------------------------|----------------|--------------|-----------------|-------------|----------------|
|                                              | Wood Chips     | Wood Pellets | ASR Batch 2     | ASR Batch 3 | Wood Pellets   |
| Moisture (wt% as received)                   | 38.1           | 8.1          | 1.6             | 1.4         | 8.5            |
| Ash (wt% dry-basis)                          | 0.5            | 0.4          | 37              | 32          | 0.4            |
| Cl (wt% dry-basis)                           |                |              | 0.63            | 0.64        |                |
| S (wt% dry-basis)                            |                |              | 0.24            | 0.19        |                |
| C (wt% dry-basis)                            | 50.2           | 50.5         | 42.0            | 47.0        | 50.4           |
| H (wt% dry-basis)                            | 6.0            | 6.1          | 5.0             | 5.4         | 6.2            |
| N (wt% dry-basis)                            | 0.12           | 0.07         | 1.5             | 1.6         |                |
| O (wt% dry-basis, approximate by difference) | 43.0           | 43.0         | 13              | 13          | 43.2           |
| LHV (MJ/kg, dry-basis)                       | 18.4           | 18.8         | 18.0            | 20.1        | 18.9           |

The fixed carbon and volatiles contents of the fuels used in this work are not reported in Table 2. For the ASR batches, the reason for this is that the fixed carbon produced during devolatilization was measured in a bench-scale fluidized bed reactor, to obtain a value representative of the conditions in

the Chalmers gasifier. Concerning the wood fuels, their fixed carbon contents were determined through TGA and showed some slight differences across the experimental campaigns. However, the heating rate in TGA is very low compared to that in a fluidized bed. Therefore, in the fluidized bed environment, the extremely high heating rates will not produce the same amount of char, and there is no telling that differences emerging from the TGA tests would emerge in similar ways, if at all, from a fluidized bed. For this reason, it was instead assumed that all wood pellets converted in the Chalmers gasifier produce the same amount of char, i.e., 16% on a mass basis.

The compositions of the ashes obtained from the combustion of wood chips, wood pellets, and ASR are shown in Table 3. These values are mainly of interest for the biomass used in **Paper I**, in which the accumulation of certain ash species in the bed material was assessed. While the composition of the ash from ASR was not used in **Paper II**, it is nonetheless of interest, to relate the bed composition (given in Table 1) to the accumulation of ASR ash. It should also be noted that, as expected based on its origin, the ASR ash is rich in metals such as Fe, Zn, and Cu.

**Table 3.** Elemental compositions of the ashes derived from combustion of the biomass and ASR fuels used in this thesis.

|         | Wood chips                       | Wood pellets | ASR Batch 2                      | ASR Batch 3 |
|---------|----------------------------------|--------------|----------------------------------|-------------|
| Element | Concentration (mg/kg, dry-basis) |              | Mass percent, dry-basis          |             |
| Al      | 20                               | 50           | 1.6                              | 1.5         |
| Si      | 80                               | 150          | 4.8                              | 4.2         |
| Fe      | 20                               | 30           | 8.3                              | 6.8         |
| Ti      | <10                              | <10          | 0.45                             | 0.43        |
| Mn      | 70                               | 13           | 0.10                             | 0.08        |
| Mg      | 230                              | 210          | 0.51                             | 0.48        |
| Ca      | 1200                             | 950          | 2.3                              | 2.1         |
| Ba      | 20                               | 10           | 0.34                             | 0.31        |
| Na      | 40                               | 30           | 0.59                             | 0.49        |
| K       | 670                              | 460          | 0.34                             | 0.33        |
| P       | 80                               | 70           | 0.28                             | 0.29        |
| Br      |                                  |              | 0.30                             | 0.42        |
|         |                                  |              | Concentration (mg/kg, dry-basis) |             |
| As      |                                  |              | 9                                | 14          |
| Cd      |                                  |              | 10                               | 9           |
| Co      |                                  |              | 750                              | 37          |
| Cr      |                                  |              | 1,400                            | 400         |
| Cu      |                                  |              | 5,800                            | 5,500       |
| Mo      |                                  |              | 110                              | 37          |
| Ni      |                                  |              | 730                              | 260         |
| Pb      |                                  |              | 660                              | 600         |
| V       |                                  |              | 32                               | 25          |
| Zn      |                                  |              | 15,500                           | 13,800      |

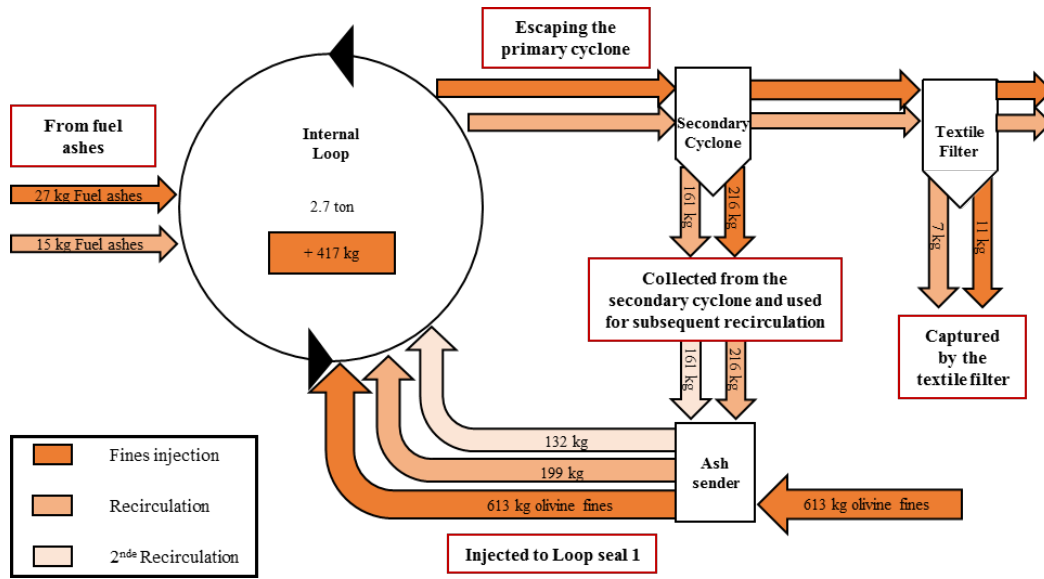
# Chapter 4: Enhancing carbon recovery in the form of valuable products: circulation of flue gas coarse ash

## 4.1. Rationale

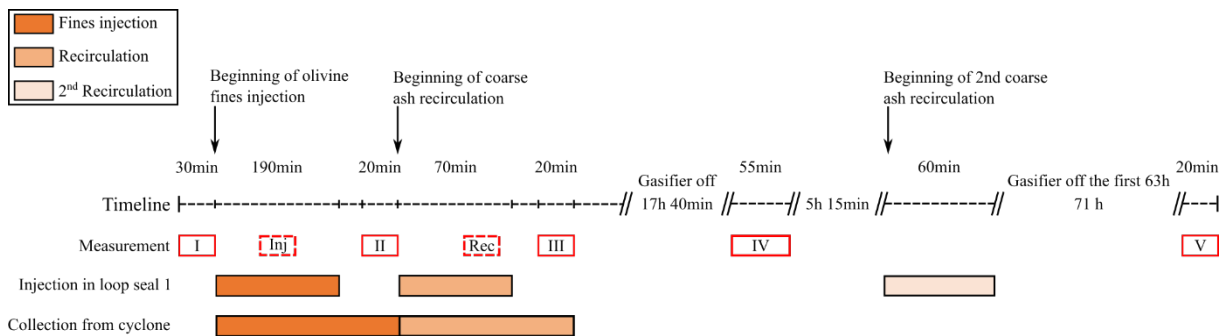
The focus of this chapter is an investigation of the impact of the circulation of the flue gas coarse ash on the catalytic activity in a DFB gasifier. Typically, in existing DFB gasifiers, the flue gas ash is not continuously circulated back to the internal loop, and the circulation step is performed with the goal of reducing the need for bed material make-up feeding. However, this stream contains potentially active species such as AAEM, in the form of fragments of the ash layer of the bed material, as well as ash components introduced with the gasifier fly ash, which is circulated to recover the energy content of the char fines. The circulation of the flue gas ash could, therefore, represent a way to enhance the catalytic activity in the gasifier and, thereby, increase carbon recovery in the form of valuable products.

## 4.2. Method

In order to be able to study the effect of flue gas ash circulation on the activities in the Chalmers DFB gasifier, the production of fly ash had to be stimulated so as to generate detectable effects. This was achieved by injecting untreated olivine in a fine fraction into loop seal 1. From this injection, fly ash was collected from the secondary cyclone used to collect flue gas coarse ash. The collected coarse ash was circulated back to loop seal 1 one time, collecting the resulting coarse ash, which was then recirculated for a second time. A detailed description of the injection and recirculation flows is given in **Paper I** and is summarized here in Figure 8. Based on the injections and subsequent recirculation steps, five experimental cases carried out under stable conditions were established, as well as two transient cases. For each of these cases, permanent gas measurements and tar sampling were carried out. In connection with the stable measurements, solid samples were also collected. The timeline for the experiments and related measurement periods is depicted in Figure 9, in which a color code matching that used in Figure 8 is used to represent the olivine fines injections and the two rounds of coarse ash circulation. The experimental cases are described in Table 4, along with the operational conditions prevailing during the measurements.



**Figure 8.** Mass flows following the olivine fines injection and subsequent coarse ash recirculation. The internal loop refers to the bed material circulation between the gasifier and the combustor. The time sequence for the injection and recirculation steps is shown in Figure 9.



**Figure 9.** Timeline of the experimental campaign. The olivine fines injections and subsequent coarse ash recirculation steps are indicated, as well as the periods of collection of coarse ashes from the secondary cyclone. The five stable measurement cases (I to V) are represented as red continuous boxes, while the two transient measurement cases, “Inj” and “Rec”, are represented by red dashed boxes. These cases are also summarized in Table 4. The durations of the injections and stable measurements are shown on the timeline. “Gasifier off” means that no fuel is fed to the gasifier, and it is instead fluidized with the combustor flue gases. The extents of the events are not shown to scale.

**Table 4.** Summary of the experimental cases investigated in **Paper I**.

| Day | Experimental Case | Description                 | Solid samples    | Temperature in the bed (°C) | Fuel flow (kg/h) | Fluidization level (kg/h) |
|-----|-------------------|-----------------------------|------------------|-----------------------------|------------------|---------------------------|
| 1   | I                 | Reference                   | Coarse ash + Bed | 809                         | 295              | 160                       |
|     | Inj 1–4           | During fines injection      |                  |                             |                  |                           |
|     | II                | After fines injection       | Coarse ash       | 822                         | 296              | 160                       |
|     | Rec 1–4           | During recirculation        |                  |                             |                  |                           |
| 2   | III               | After recirculation         | Coarse ash + Bed | 819                         | 295              | 160                       |
|     | IV                | Before second recirculation | Bed              | 817                         | 291              | 160                       |
| 5   | V                 | After regeneration          | Bed              | 829                         | 296              | 160                       |

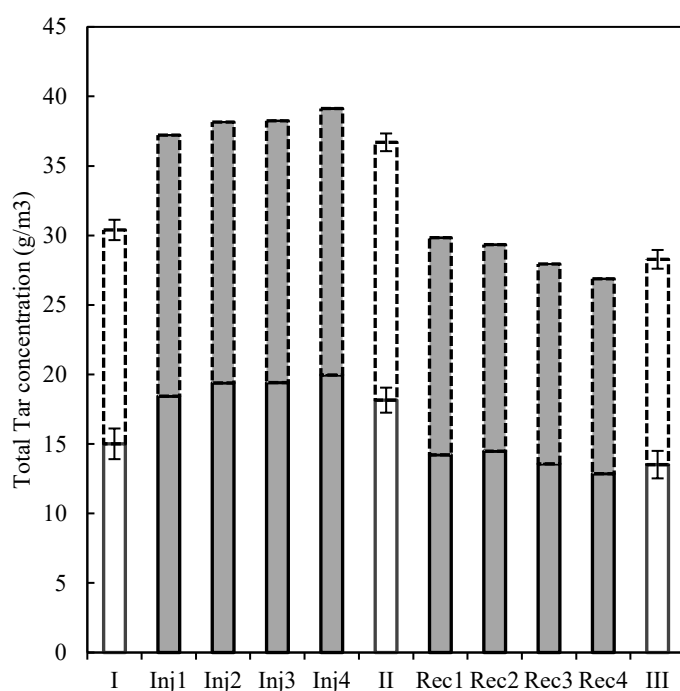
Three aspects of the impact of coarse ash circulation on the gas quality and tar quality were assessed: (i) the immediate and short-term effects of the ash circulation on the gas and tar compositions; (ii) the long-term effects persisting after recirculation; and (iii) the resilience of these effects to bed regeneration. The immediate effect of coarse ash circulation on the concentration of tar in the raw gas was determined by sampling the tar during the circulation and comparing the concentrations obtained with a reference case, Case I, which was established prior to the injection of olivine fines into the system. A measurement was taken under stable conditions once the circulation had been completed, to assess whether any observed effect remained in the short-term (Case III). Since the injection of a large amount of untreated olivine fines into the system can be expected to cause changes, especially considering that more than 400 kg of olivine fines were retained in the bed, a stable measurement was taken after the injection (Case II). Sampling of tar during the injection of olivine fines was also carried out.

The long-term effect of coarse ash circulation was assessed by comparing Case IV to Case III. To distinguish the potential activation effect of the coarse ash on the bed from the natural activation that is known to take place with time through interaction with the fuel ash, the results were compared with tar measurements from an olivine aging experiment that was previously carried out in the same system, under similar conditions and with the same type of olivine [41]. In that experiment, replacement of the olivine bed with 800 kg of untreated olivine was performed, corresponding to replacement of about 24% of the inventory. A similar bed replacement was carried out in the work presented in **Paper I**, although the amount of untreated olivine replaced was double that in the aforementioned reference experiment. Therefore, comparison of the activities of the beds in the two experiments, *via* the tar yields, is used to elucidate whether coarse ash circulation has an impact on the resilience of the bed activity to regeneration.

### 4.3. Results

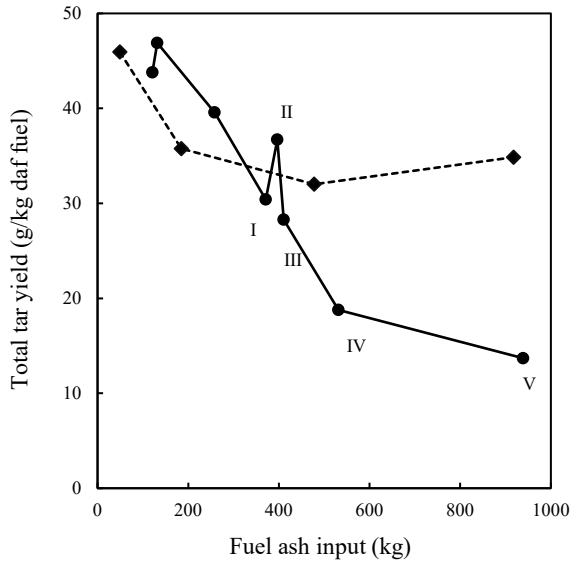
The immediate and short-term effects of coarse ash circulation on the tar concentration (including BTX) in the gasifier's raw gas is shown in Figure 10. Initially, the injection of cold, inactive olivine fines led to an increase in the tar concentration, which persisted after the injection was completed, due to the retention of more than 400 kg of those fines in the bed. The circulation of the coarse ash generated from this injection of olivine fines immediately resulted in a decrease in tar concentration,

which remained lower than that in Cases I and II once the circulation was over. Since the coarse ash was produced from a stream that is known to have exited the gasifier, the decreased tar concentration cannot be explained by the retention of coarse ash particles in the bed. Instead, it suggests that their circulation had increased the activity of the bed towards tar conversion, possibly by transferring active ash components to the bed particles. Nonetheless, it was found that oxygen transport was higher in Case III than in Case I, which indicates that oxidation of tar species also contributes to the lower tar concentration.



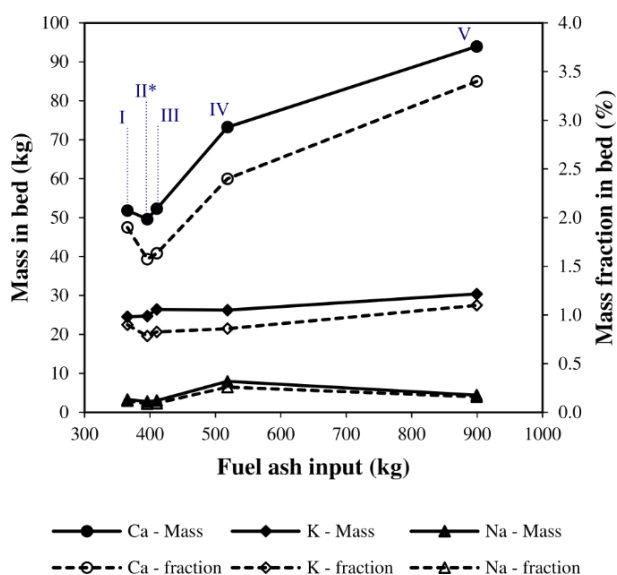
**Figure 10.** Tar concentrations before, during, and after the injection of olivine fines and the first round of coarse ash recirculation. The light shading indicates measurements averaged over a stable period, whereas the dark shading represents the tar samples taken during the olivine fines injections (Inj 1–4) and the coarse ash recirculation steps (Rec 1–4). The dashed boxes represent the BTX fraction (including unknown species with nearby retention times). For stable measurements, the standard deviations are indicated by error bars. The concentrations are given under *Normal* conditions, i.e., at atmospheric pressure and at a temperature of 20°C.

The long-term effect of ash circulation can be revealed by comparing the change in activity towards tar conversion from Case III to Case IV with the change in activity expected from “regular” ageing of the bed. The ash-circulation and the reference experimental campaigns are compared on the basis of fuel ash fed to the system, excluding the coarse ash input. It is clear that the activity of the reference case leveled off at an ash input of approximately 500 kg, at an activity level comparable to that in Case III. Conversely, the activity in the ash-circulation experiments continued to increase, at a rate comparable to the early activity increase, despite no additional circulation of coarse ash between Cases III and IV. This shows that the previous coarse ash circulation permanently and profoundly increased the activity level of the bed material. From Case IV to Case V, after a second round of coarse ash circulation, and more importantly, extensive bed replacement, the activity increased further. This is in contrast to the reference case, in which bed replacement of lower magnitude led to a loss of activity for the overall bed. In summary, the coarse ash circulation’s effect on bed activity was three-fold, increasing the activation rate, the activation level, and the resilience to deactivation.

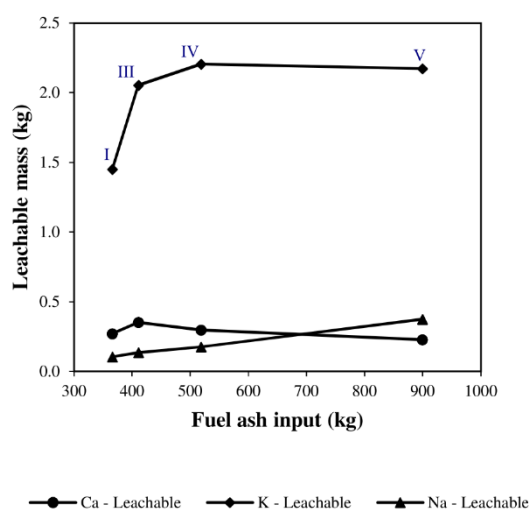


**Figure 11.** Evolution of the total tar yield (including BTX) with the cumulative fuel ash input (not accounting for coarse ash circulation). Comparison with an aging experiment is indicated by the dashed line. The Roman numerals indicate the five stable experimental cases.

This effect on the activity of the bed material was linked to the accumulation of ash components in the bed, notably active species, such as Ca, K and Na. Figure 12 shows that the Ca content of the bed increased significantly with time (as fuel ash input), following the trend for activity. The amount of leachable K from the bed was found to follow the activity and increased substantially after the first round of coarse ash circulation. These results indicate that both Ca and K contribute to the increased activity, most likely due to the former being present in the ash layer and the latter having mobility and being present in the gas phase. This is consistent with results in the literature related to the roles of alkali and alkali-earth metals in gasification. Furthermore, synergetic effects of Ca and K in the ash layer, as proposed by Knutsson *et al* [52], are consistent with the results shown here. The trend for Na indicates that it may also be involved in gas-phase catalysis, as its leachable mass increased in line with the activity.



**Figure 12.** Calculated masses of calcium, potassium and sodium in the bed plotted against the fuel ash input. The values are based on a mass balance, and the mass fractions are obtained from the ICP-OES analysis of the bed material. Point II\* does not correspond to an actual bed sample but is instead an estimation.



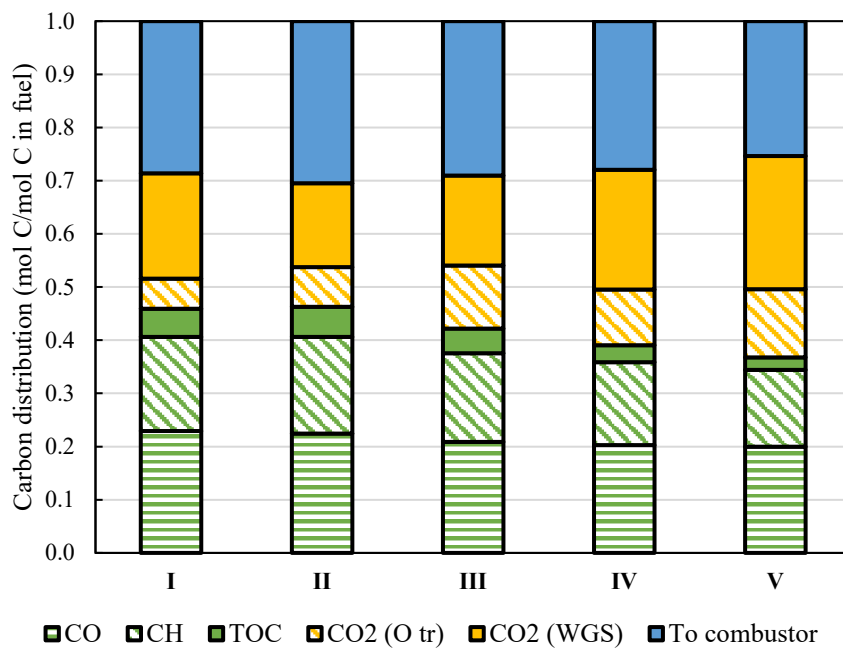
**Figure 13.** Estimated leachable masses of calcium, potassium, and sodium, determined from the leaching analysis and mass balances.

The accumulation of these active ash components in the bed is attributed to their transfer from the circulated coarse ash. Compared with the initial injection of olivine fines, which stimulated their production, the coarse ash was found to enrich for ash components, notably Ca, K and Na, after each round of circulation. Analysis of the K in the coarse ash compared with a reference (coarse ash collected prior to injection of olivine fines) showed that the fraction of leachable K was much higher. This suggests that the coarse ash particles act as condensation seeds as they pass through the cooling sections of the system. Consequently, the role of the coarse ash when it is circulated in the DFB loop, beyond its direct catalytic effect, is to redistribute active species that can subsequently interact with the bed or the gas phase.

Although a clear improvement in tar abatement can be regarded as beneficial for the process, it is important to consider how the carbon converted from the tar is distributed into other products. Figure 14 shows the carbon distributions for the five cases investigated. The carbon in the CO<sub>2</sub> from the raw

gas is divided into that produced from the WGS reaction and that generated from the reaction with transported oxygen. As it is not possible to know in what form the carbon was prior to reaction with the lattice oxygen, the maximal amount of CO<sub>2</sub> from the reaction is shown, i.e., the CO<sub>2</sub> formed from the reaction of CO with lattice oxygen. It is assumed that half of the transported oxygen reacts in this way with CO, while the other half reacts with H<sub>2</sub>. Assuming maximal CO<sub>2</sub> formation by oxygen transport is reasonable, as CO is the carbon-containing gas species that is most likely to react with the lattice oxygen, owing to the small size of the molecule compared to hydrocarbons and its predominance in the gas phase. Following the same reasoning, a direct reaction of the tar with lattice oxygen is highly unlikely.

Figure 14 shows that the tar conversion did not lead to an increased amount of carbon in the forms of CO and light hydrocarbons. Instead, the carbon was transferred to the CO<sub>2</sub> in the raw gas. This transfer of carbon occurs *via* both the WGS reaction and oxygen transport, although the carbon produced from the former follows the activity trend better. Regarding oxygen transport, the circulation rates of the bed material were similar in Cases I, IV and V. This indicates that the increased oxygen transport is imputable to the accumulated ash components' interactions with the bed material. This means that, as ash components interact with and accumulate on the bed particles, they induce not only an increase in activity towards tar reforming, but also towards the WGS reaction, as well as an increase in oxygen transport. Taken together, this results in a net transfer of carbon to the CO<sub>2</sub> in the raw gas.

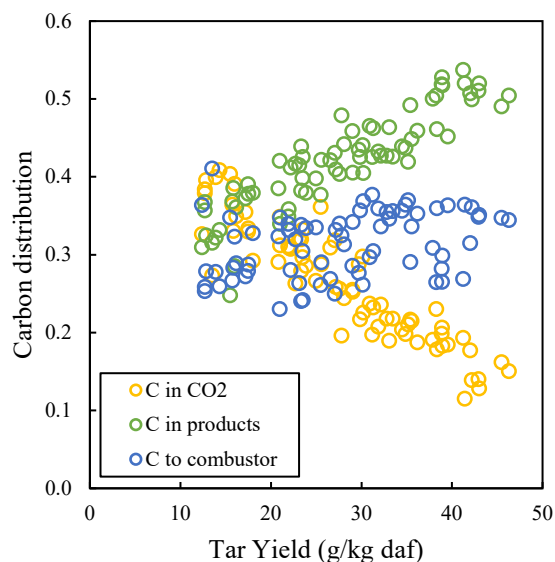


**Figure 14.** Carbon distributions for the five cases. The blue bars represent the carbon going to the combustor as unconverted fuel from the gasifier. The yellow bars represent carbon in the form of CO<sub>2</sub> in the raw gas, and the green bars represent the carbon in the products. For the carbon in the form of CO<sub>2</sub>, a distinction is made between the estimated CO<sub>2</sub> formed from the WGS reaction (filled bar) and that formed from oxygen transport (diagonal pattern). The carbon in the products is divided into carbon as TOC (filled bar), carbon as light hydrocarbons (diagonal pattern), and carbon as CO (horizontal pattern).

#### 4.3.1. Activation and carbon distribution

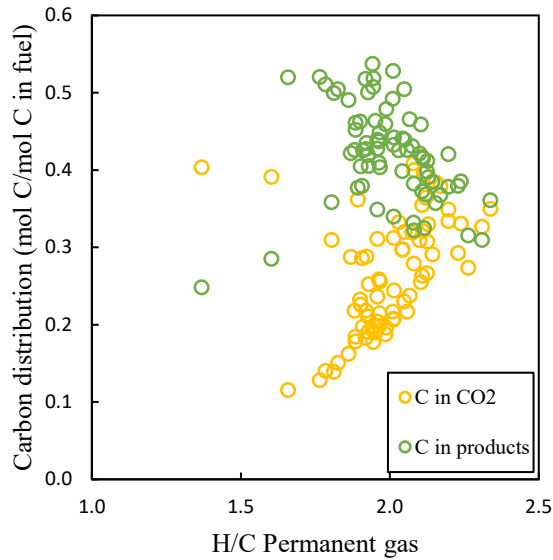
The transfer of carbon from products to CO<sub>2</sub> with increased activity resulting from coarse ash circulation can be generalized, regardless of the activation mechanism. This was investigated for wood

pellet gasification with olivine and feldspar, two materials that are known to develop significant catalytic activity in a DFB gasifier. The carbon distributions into products (including all organic compounds), CO<sub>2</sub> in the raw gas, and CO<sub>2</sub> released in the combustor, are shown against the tar yield and the H/C ratio of the permanent gas in Figure 15 and Figure 16, respectively. The H/C ratio is chosen as a marker of catalytic activity, since the reforming and gasification reactions add more hydrogen than carbon to the permanent gas, and the WGS reaction adds only hydrogen.



**Figure 15.** Carbon distributions into CO<sub>2</sub> in the raw gas (yellow), products (green), and CO<sub>2</sub> released in the combustor (blue), plotted against the tar yields for various measurement points obtained from the Chalmers gasifier, with olivine and feldspar as bed materials.

The trends evident in Figure 15 are unequivocal: with increasing activity towards tar conversion, a clear transfer of carbon occurs from the products to CO<sub>2</sub>. A slight decrease in the amount of carbon circulating to the combustor in the presence of increasing activity is also seen. The same transfer from products to CO<sub>2</sub> is seen with increased activity in Figure 16, although the data-points are more broadly scattered. These results are consistent with the findings reported in the literature for the effect of activation (*via* layer formation) on catalytic activity and the resulting effects on the product of a DFB gasifier, as discussed in *Section 1.2.2*. As the reforming reactions of tars and their precursors are intensified, carbon is transferred to CO and light hydrocarbons. The catalytic activity of AAEM towards the reforming of light hydrocarbons and the WGS reaction causes a transfer of carbon from the light hydrocarbons to CO to CO<sub>2</sub>. The increased activity may also cause a decrease in carbon transfer to the combustor. However, this is limited by the heat balance of the system. Moreover, intensification of the gasification and reforming reactions is expected to cause an increase in the heat demand of the gasifier.



**Figure 16.** Carbon distributions into CO<sub>2</sub> in the raw gas (yellow) and products (green), plotted against the H/C ratio of the permanent gas, with olivine and feldspar as bed materials.

The implications of these results are significant for the design and operation of DFB process. First, achieving the highest possible catalytic activity cannot be the end-goal in the optimization of all DFB processes, in the absence of a clear plan, as well as the capacity, to recover the CO<sub>2</sub> from the raw gas and valorize its carbon, either chemically or by sequestration. Figure 15 and Figure 16 show that, at high activity levels, there is as much or more carbon in CO<sub>2</sub> than in the products. Thus, the CO<sub>2</sub> stream cannot be considered as simply a side-product. Second, it may be worthwhile to aim for lower activity levels and to apply more robust and sophisticated methods for downstream tar removal. However, the desired product from biomass gasification is, in most cases, a syngas with a specific H<sub>2</sub>/CO ratio. This means that a reforming reactor and a WGS reaction are generally used to reform fully the raw gas and adjust the H<sub>2</sub>/CO ratio. Consequently, the issue of having too high an excessive activity in the gasifier becomes a strength, as it reduces the demand on these two reactors. Still, the CO<sub>2</sub> concentration at the inlet of the WGS reactor may be too high to obtain the desired H<sub>2</sub>/CO ratio, due to oxygen transport in the gasifier.



# Chapter 5: Carbon-free heat production in the combustor: the case of CLG of biomass and waste

As explained in Chapter 1, while regular DFB gasification relies on the combustion of part of the fuel fed to the gasifier and results in the production of a flue gas with a low concentration of CO<sub>2</sub>, the CLG technology is designed to segregate all the carbon to a single reactor, the FR. Moreover, the use of waste materials as oxygen carriers in the CLG process, either directly or through the creation of an oxygen-carrying bed from a waste fuel ash, can alleviate many of the material issues associated with technologies that rely on oxygen carriers. Nonetheless, as detailed in Chapter 2, several other challenges must be overcome for CLG to become viable. This chapter investigates the optimization of CLG, here in a case in which waste-derived oxygen carriers are used. Nonetheless, most of the results obtained and conclusions drawn can be generalized to other oxygen carriers, since many of the issues are related to the optimization of process parameters.

## 5.1. CLG of biomass using LD slag as oxygen carrier

Controlling the oxygen transport through the use of a bed material is crucial for the viability of the CLG process. Indeed, in CLG, the oxygen transport controls the heat production in the AR, although it oxidizes the products in the FR, which can greatly limit the value of the outputs of the process. The most sensible way to express the oxygen transport is as the ratio of oxygen transported to the oxygen required for complete combustion of the fuel, as this is indicative of how much fuel is available for oxidation. When defined in this way, the oxygen transport is governed by two factors: the oxygen-carrying capacity of the bed; and the ratio of the bed material flow to the fuel flow (bed-to-fuel ratio). The former imposes a limit on the oxygen transport for a given bed-to-fuel ratio and is determined by the following: how reductive the atmosphere in the FR is; the gas-oxygen carrier contact; the temperature in each reactor; and the bed material composition. Controlling the oxygen transport is, therefore, achieved by controlling either or both of the oxygen-carrying capacity and the bed-to-fuel ratio.

This was the aim of **Paper A**, which investigated how diluting the oxygen-carrying bed with silica sand and reducing the bed-to-fuel ratio functioned as control methods for the oxygen transport. As measures of the success, or lack thereof, of these methods, the CGE, the degree of char conversion, and the tar yield were used. The CGE represents the energy recovered in the permanent gas as combustible species, which are generally considered valuable. Regarding the degree of char conversion, it is important to note that as the Chalmers gasifier is not designed for CLG, achieving complete char conversion is not possible. Nonetheless, even in a DFB that is specifically designed and optimized for CLG, complete char conversion remains a challenging goal. Moreover, the transport of oxygen by the bed is known to enhance char gasification. As a consequence, it is important to investigate how controlling the oxygen transport affects the degree of char conversion.

In this thesis, two control methods were investigated with three oxygen carriers: a manganese ore, an ilmenite ore, and LD slag. This allowed for the evaluation of the behaviors of these oxygen carriers in the CLG process, and elucidated whether the control methods have similar effects with the different oxygen carriers. In addition, this facilitated comparisons of the features of a waste-derived oxygen-carrying bed material, LD slag, with those of established oxygen carrier ores. The oxygen carriers were also compared with two bed materials: silica sand, and an active olivine. The former served as a

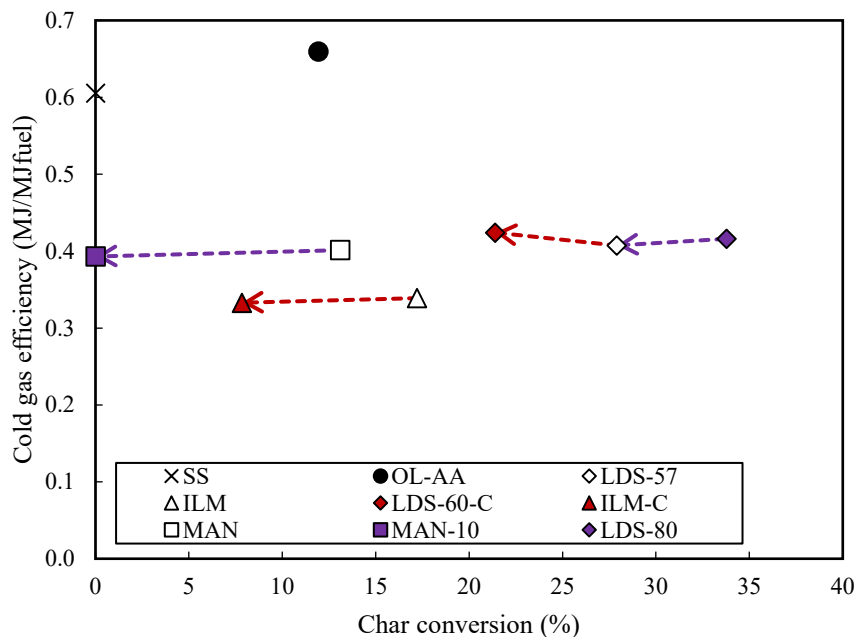
reference inert material, while the latter corresponds to a very active bed material, with a low oxygen-carrying capacity (as compared to the oxygen carriers). The compositions of the five bed materials are listed in Table 1. Dilution of the oxygen carrier was carried out for the LD slag and manganese, and reduction of the bed-to-fuel ratio was carried out for LD slag and ilmenite. This results in a total of nine experimental cases, which are described in Table 5, with the tag they are referred, the operational conditions, and the fraction of silica sand in the bed, for the oxygen carriers. The reference measurements were: LDS-57 for LD slag; ILM for ilmenite; and MAN for manganese. The dilution experiments compared LDS-80 to LDS-57 for LD slag, and MAN to MAN-10 for manganese. The decrease in bed-to-fuel ratio experiments compared LDS-57 to LDS-60-C for LD slag, and ILM to ILM-C for ilmenite.

**Table 5.** Operational conditions for the nine measurement cases investigated in **Paper A**. The tags that are used to refer to each measurement in the remainder of the Chapter are listed.

| Material                        | Tag      | Fuel flow (kg/h) | Circulation rate (tonnes/h) | Steam to fuel mass flow ratio | Gasifier temperature (°C) | Fraction of silica sand (for oxygen carriers) |
|---------------------------------|----------|------------------|-----------------------------|-------------------------------|---------------------------|-----------------------------------------------|
| Silica Sand                     | SS       | 300              | 13.9                        | 0.85                          | 800                       |                                               |
| Olivine, artificially activated | OL-AA    | 296              | 10.3                        | 0.80                          | 830                       |                                               |
| LD slag 57%                     | LDS-57   | 305              | 24.3                        | 0.81                          | 825                       | 43                                            |
| LD slag 80%                     | LDS-80   | 304              | Not measured                | 0.79                          | 825                       | 20                                            |
| LD slag 60%                     | LDS-60-C | 400              | 15.5                        | 0.63                          | 810                       | 40                                            |
| Ilmenite                        | ILM      | 284              | 22.1                        | 0.81                          | 826                       | 0                                             |
| Ilmenite                        | ILM-C    | 380              | 10.4                        | 0.76                          | 813                       | 0                                             |
| Manganese                       | MAN      | 304              | 16.6                        | 0.84                          | 808                       | 0                                             |
| Manganese                       | MAN-10   | 304              | 19.4                        | 0.83                          | 815                       | 90                                            |

### 5.1.1. Controlling oxygen transport: impacts on CGE, char conversion, and tar yield

The CGE and char conversion are shown for the nine cases in Figure 17. The data have been re-evaluated (compared with the results shown in **Paper A**) by applying the assumption that the wood pellets used in all nine cases produced the same amount of char in the FR, as described in *Section 3.5.2*.



**Figure 17.** Cold gas efficiencies and char conversion rates for the nine experimental cases. Symbols: cross, silica sand (SS); circle, artificially activated olivine (OL-AA); diamond, LD slag (LDS); square, manganese (MAN); and triangle, ilmenite (ILM). The tags for the bed materials are listed in Table 5. The purple arrows represent the effects of dilution, and the red arrows represent the effects of decrease in the bed-to-fuel ratio.

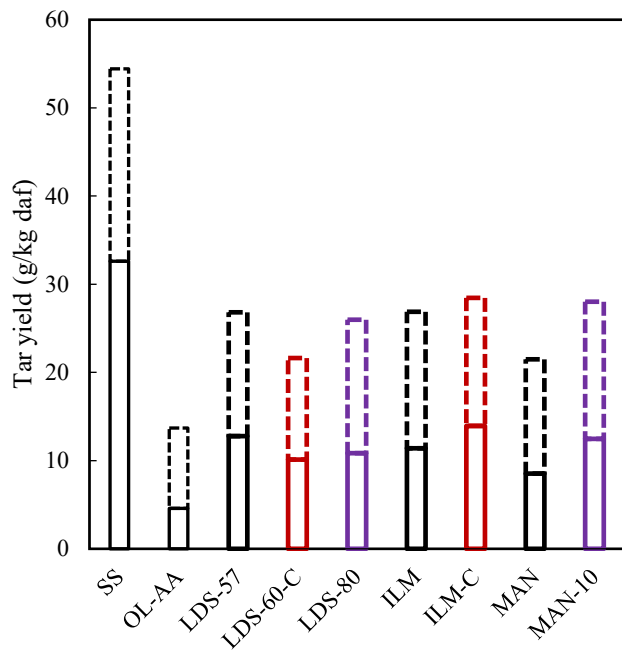
The most immediately obvious result from Figure 17 is that the cold gas efficiencies obtained with the oxygen carriers are much lower than those seen for silica sand and olivine as bed materials. This reflects the fact that the transported oxygen reacts with combustible gases in the FR, mostly  $H_2$  and  $CO$ , which decreases the energy content of the permanent gas. Interestingly, neither the reduction in bed-to-fuel ratio nor dilution with silica sand caused a significant increase in the CGE. Conversely, the attempts to reduce the oxygen transport resulted in a dramatic decrease in char conversion. This indicates that the decrease in the removal of gasification inhibitors is more important than the longer residence time of the bed, and thereby of the fuel, in the reactor.

This also suggests that the oxygen-carrier particles tend to be located on top of the bed, whereas silica sand remains within the deep bed, where fuel particles tend to gasify. When the oxygen carrier is replaced with sand, the gasifying fuel particles find themselves surrounded by sand, which does not prevent the inhibition of gasification, while the oxygen carrier particles on the top of the bed and projected in the freeboard still oxidize the volatiles and gasification products. This is most likely true particularly for the manganese ore, since even at concentrations of 10%, the CGE remains as low as at it is at 100% concentration, whereas the overall char gasification drops to zero. That this is a result of differences in fluidization behavior is supported by the fact that, despite their higher density than silica sand, the manganese particles had a lower size distribution, which resulted in a lower minimum fluidization velocity. Nonetheless, the circulation rate for MAN-10 was slightly higher than that for MAN, which contributed to the loss of char gasification.

Figure 18 shows the tar yields for the nine cases studied. It is clear that the use of oxygen carriers leads to much lower tar yields, as compared to the inert case. However, tar levels that are as low as those obtained with the active olivine are not reached. As the oxidation of tar by transported oxygen is unlikely, the lower tar yields are probably due to the catalytic activities of the metals in the oxygen

carriers, as well as calcium in the case of LD slag. Dilution of the oxygen carriers led to only a slight increase in the tar yield, which is consistent with the replacement of part of the bed with inactive material. Nonetheless, it is remarkable that when the bed only contained 10% manganese the tar yield was still as low as the cases with 100% ilmenite, with a total tar yield that was half of that obtained with silica sand. This non-linear behavior further supports the notion that manganese particles become segregated to the top of the bed, where devolatilization occurs. These results show that the bed dynamics is an important consideration in CLG when mixtures of bed materials are used (or produced from the fuel ash).

Regarding the effect of a decreased bed-to-fuel ratio, the trends for LD slag and ilmenite were opposite. In both cases, the increased fuel flow was expected to shorten the residence times of the gases in the FR, which would increase the tar yield. In contrast, the decrease in bed-to-fuel ratio caused the bed to evolve into an overall more-reduced state, which would be expected to lead to a higher catalytic surface area. The difference in tar yield that followed the lower bed-to-fuel ratio suggests that the oxidation state reached with LD slag does not provide oxygen, but instead catalyzes tar reforming and cracking reactions, whereas the lower oxidation state of ilmenite can still emit oxygen. It is also possible that the LD slag concentration, which is based on approximate estimations, was in reality higher than 60%.

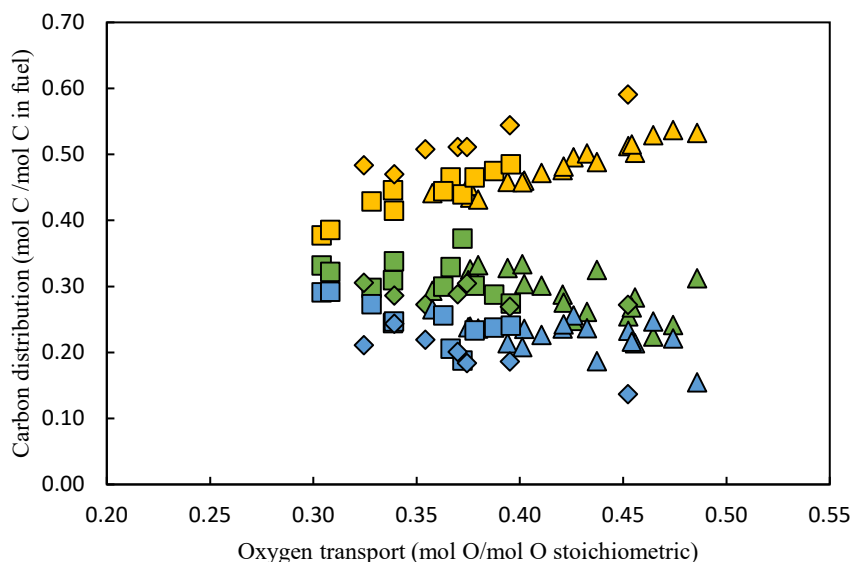


**Figure 18.** Tar yields for the nine experimental cases. Dashed bars represent the yield of Benzene, Toluene, and Xylene (BTX). The purple bars depict experiments in which the concentration of oxygen carrier was changed, and the red bars depict experiments in which the bed-to-fuel ratio was changed. The tags for the bed materials are listed in Table 5

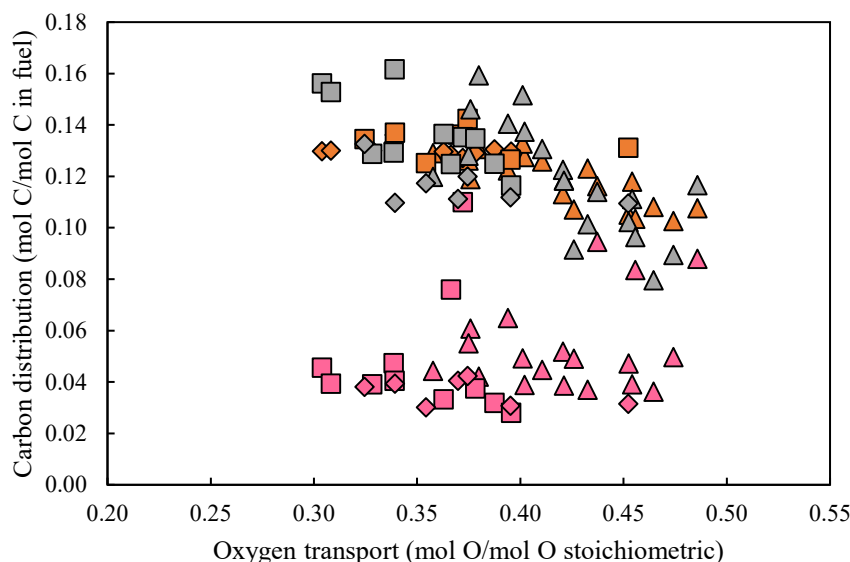
### 5.1.2. Influence of oxygen carriers on the carbon distribution in CLG

Figure 19 displays the carbon distributions into products, CO<sub>2</sub> in the raw gas, and carbon to the AR, for all the experimental cases out with LD slag, ilmenite, and manganese in the Chalmers gasifier. Figure 20 shows the carbon distributions into products, divided into TOC, carbon in CO, and carbon as light hydrocarbons. From Figure 19, a clear trend appears: the carbon into CO<sub>2</sub> in the raw gas increases linearly as the oxygen transport increases. A decreasing trend is seen for the carbon in the

products and the carbon to the combustor. Although scattered, the carbon distributions in Figure 20 reveal a decreasing trend with increasing oxygen transport for the carbon in CO and, to a lesser extent, for light hydrocarbons. The trend is particularly strong at higher oxygen transport levels for ilmenite. Conversely, the carbon in organic compounds with more than four carbon atoms remains relatively stable with increasing oxygen transport, concentrating 4%–6% of the carbon from the fuel.



**Figure 19.** Distributions of carbon to the products (green), to the combustor (blue), and to the CO<sub>2</sub> in the raw gas (yellow) as a function of the oxygen transport. The squares represent manganese, diamonds represent LD slag, and triangles represent ilmenite.



**Figure 20.** Distributions of carbon to: the products, CO (gray), light hydrocarbons (orange), and TOC (pink), as a function of the oxygen transport. The squares represent manganese, diamonds represent LD slag, and triangles represent ilmenite.

These results indicate that the transported oxygen reacts mainly with CO among the carbon species and, therefore, the partial oxidation of hydrocarbons, in particular tar, is limited. Consequently, if oxygen carriers are used in the DFB to take advantage of the transition metals' catalytic activities for

gas reforming and tar abatement, much lower levels of oxygen transport than those investigated in the present work are required. However, the problem of the fulfillment of the heat balance, which was not investigated here, must still be resolved. That is to say, if low oxygen transport levels are desired to ensure high carbon recovery in valuable products, a high CGE, and a low tar content, then combustion of part of the products or char may be needed to fulfill the heat balance. This brings into question the rationale for using oxygen carriers at all; in such a case, catalytic, non-oxygen-carrying bed materials may be preferable.

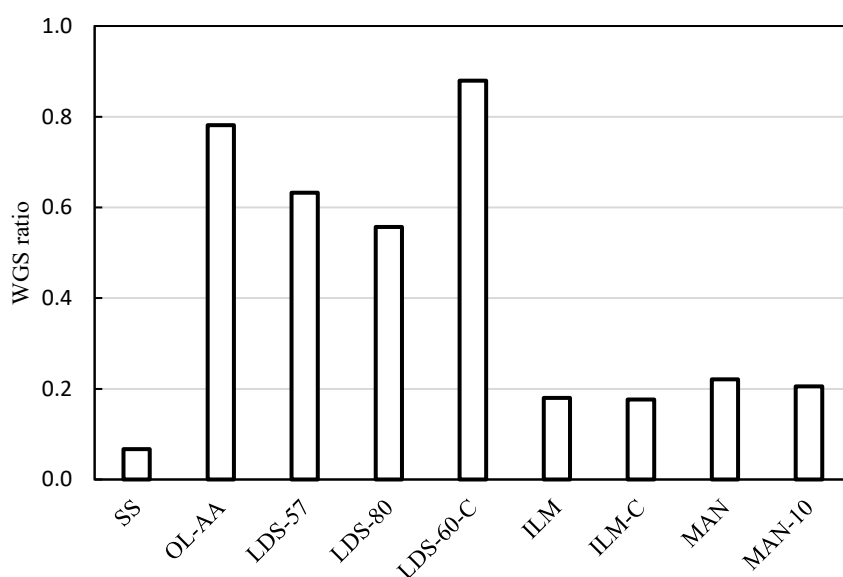
Nevertheless, under specific conditions, carbon recovery into a single, undiluted stream may have sufficient value in itself to justify using oxygen carriers and aiming for CLG. A low rate of carbon recovery as products and a high rate of recovery as CO<sub>2</sub> may be acceptable if there is a value assigned to the sequestration of CO<sub>2</sub>. Concerning the products, a significant amount of organic compounds, including tar, remains, and this will likely require downstream upgrading (such as steam reforming) to avoid operational issues. In addition, it should be noted that producing syngas with a specific H<sub>2</sub>/CO ratio may be challenging due to the high CO<sub>2</sub> content of the raw gas. Ultimately, the value of the CLG method for the simultaneous sequestration of carbon and production of a valuable raw gas must be assessed through comparison with the alternative, i.e., DFB gasification with oxy-combustion on the AR side.

The feasibility of the operation of the DFB in actual CLG mode requires the achievement of complete carbon conversion in the FR, which remains a challenge. Although the oxygen transport contributes to improving the rate of char conversion, the amount of unconverted carbon leaving the FR is high even at high oxygen transport levels. Besides, as described in *Section 5.1.1*, improving the fuel conversion by modulating the oxygen transport is at odds with the production of a high-value gas and (see Figure 19) with the recovery of carbon in the form of products. However, the low rates of char conversion observed in the reported experiments can be attributed, to a large extent, to the design of the Chalmers DFB system. Indeed, several design decisions can be taken to allow for a much higher degree of char conversion. For instance, a long fuel reactor increases the residence time while allowing for high circulation rates. Incomplete fuel conversion can be acceptable if downstream carbon separation, for instance using a carbon stripper, is carried out. The separated carbon can be fed back to the gasifier to increase the overall fuel conversion.

### 5.1.3. LD slag as a waste-derived oxygen-carrying bed material for CLG

The results presented in *Sections 5.1.1* and *5.1.2* provide an opportunity to evaluate LD slag as an oxygen carrier for CLG, as compared with ilmenite and manganese. From Figure 17, it can be seen that the use of LD slag leads to a higher degree of char conversion and a slightly higher CGE than the use of either ilmenite or manganese. Given that the oxygen transport levels for all three oxygen carriers are similar (albeit slightly higher for ilmenite), the higher degree of char conversion cannot be explained by the removal of inhibitors of the gasification reaction. The MAN experimental case was performed at a lower temperature than the ILM and LDS-57 cases, which may explain the lower gasification rate, although it also was carried out at a lower circulation rate, which would contribute to enhancing the degree of gasification. It is also possible that the difference is due to the catalytic behaviors of the materials. Given that solid-solid catalysis is unlikely, a probable explanation is that LD slag, by virtue of its lower alkali-getter ability, increases the gas-phase concentration of alkali, leading to higher gasification rates.

The gas produced by the LD slag also contains more hydrogen than the gases generated through the use of ilmenite and manganese. This can be explained by the much higher catalytic activity of LD slag towards the WGS reaction, as compared with the other two oxygen carriers, as shown in Figure 21. The ratio of the constant of the WGS reaction to its equilibrium value is comparable for LD slag and the active olivine. Conversely, ilmenite and manganese produce a gas that is only slightly closer to equilibrium compared with inert sand. This could be due to differences in catalytic activity between the transition metals and calcium, or to the fact that the oxygen-carrying and catalytic phases are separated in the LD slag. This would explain how it can provide both oxidative and catalytic surfaces (without needing reduction of the site first). Interestingly, the higher activity of the WGS reaction should contribute to an overall lower CGE of the LD slag.



**Figure 21.** Ratio of the WGS reaction quotient to its equilibrium value for each of the nine measurements. The tags for the bed materials are listed in Table 5

Given its higher activity towards the WGS reaction, using LD slag in the FR leads to a higher degree of conversion of carbon to  $\text{CO}_2$ , as shown in Figure 19. Another noteworthy result from Figure 19 is that the oxygen transport obtained with the LD slag is comparable to that obtained with ores that have demonstrated industrial potential for CLC or OCAC. This means that LD slag is a promising candidate as an alternative to ores due to its comparatively low price. However, whether or not it is a more suitable oxygen carrier depends on many considerations. Due to its higher yield of carbon as  $\text{CO}_2$ , it may be a more suitable option when carbon sequestration is favored.

## 5.2. CLG of a plastic waste, automotive shredder residue, using the generated ash as oxygen carrier

### 5.2.1. Method

In the work described in **Paper II**, thermochemical conversion of ASR by CLG was investigated in the Chalmers DFB system, under near-steady-state conditions in terms of the accumulation of ASR-ash in the bed. Although the exact bed composition is unknown, the ASR-ash can be assumed to be present in significant amounts. From the metal-rich ASR-ash, oxygen-carrying properties were found to emerge in the bed, at a greater magnitude than when the ASR was converted with a bed composed exclusively of olivine. The aim of **Paper II** was to demonstrate that CLG of ASR, using its own ash as oxygen carrier, is feasible. The issue of achieving complete fuel conversion, already partly addressed with biomass in *Section 5.1.1*, is tackled here by investigating how it is affected by the following four parameters: the circulation rate of the bed; the temperature of the FR; the fuel feeding rate; and the level of oxygen transport. Only the latter is discussed in depth in this thesis. In addition, the heat balance of the system was established to assess feasibility in a purely CLG mode, i.e., without char combustion in the AR.

For **Paper II**, 14 measurement points were used. The operating conditions covered by these measurements are listed in Table 6. In addition, the operating conditions for the three measurement points used to compare the impacts of oxygen transport on ASR conversion are given. Note that the three measurements were not taken on the same day. The 14 measurement points were acquired over a period of 5 days, corresponding to Day 9 to Day 13 of an experimental campaign conducted with ASR.

**Table 6.** Operating conditions for the three measurement points corresponding to various levels of oxygen transport. The operating conditions range is also given for the 14 measurement points.

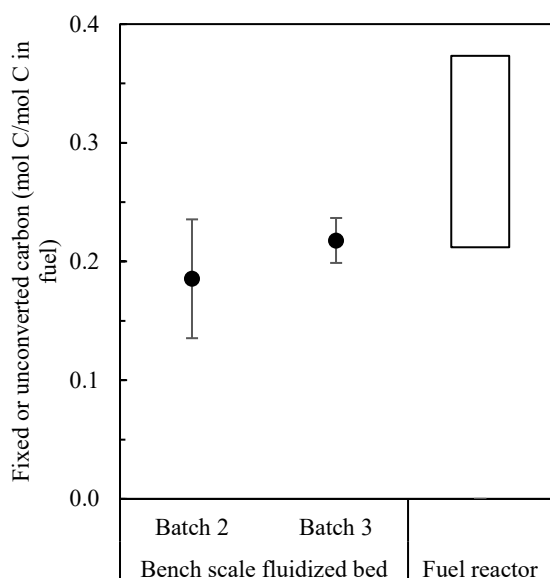
| Varied parameter            |         |    | Operating condition     |                              |                                             |                               |
|-----------------------------|---------|----|-------------------------|------------------------------|---------------------------------------------|-------------------------------|
|                             |         |    | Circulation rate (kg/h) | Fuel feeding rate (kg daf/h) | Oxygen transport (mol O/mol stoichiometric) | Fuel reactor temperature (°C) |
| Oxygen transport            | Point 1 | 13 | 18,100                  | 175                          | <b>0.22</b>                                 | 824                           |
|                             | Point 2 | 11 | 17,700                  | 174                          | <b>0.24</b>                                 | 826                           |
|                             | Point 3 | 9  | 18,000                  | 168                          | <b>0.29</b>                                 | 821                           |
| 14-measurement points range |         |    | 14,400–21,200           | 158–202                      | 0.20–0.29                                   | 790–835                       |

### 5.2.2. Results

#### 5.2.2.1. ASR conversion

Given the heterogeneity of ASR, the variability of its composition, and the limited knowledge available regarding its behavior in fluidized bed steam gasification, its devolatilization time and char formation were assessed in a bench-scale fluidized bed reactor. The amount of fixed carbon determined from bench-scale fluidized bed experiments, for the two ASR batches, were compared with the amount of unconverted carbon measured in the FR for all 14 measurement points (Figure 22). It is apparent that the conversion in the FR is limited, reaching, at best, a level of conversion corresponding only to the fixed carbon estimated from the bench reactor. This shows that the devolatilization of ASR in the FR

is incomplete. The estimates of the devolatilization time indicate that it is comparable with the expected residence time of the ASR in the FR, which suggests that a significant fraction of the particles leave the reactor without having become fully devolatilized. This is supported by the results obtained when the circulation rate of the bed material was varied. There was a slight increase in the proportion of carbon as TOC with lower circulation rates (entailing higher residence times), which can only be attributed to incomplete devolatilization.



**Figure 22.** Comparison of the amount of fixed carbon assessed in the bench-scale fluidized bed reactor with the amount of unconverted carbon leaving the Chalmers gasifier/FR. The error bar represents the standard deviation of the measurement. The unconverted carbon in the FR is depicted as a box, to distinguish the repeated measurements made under controlled conditions in the bench reactor from the measurements made in the FR, which spanned multiple operating conditions.

#### 5.2.2.2. Impacts on ASR conversion of circulation rate, fuel reactor temperature, and fuel feeding rate

As mentioned above, the impacts of the other three parameters investigated in **Paper II** are not discussed in detail in this thesis. Nonetheless, a brief account of their effects is pertinent. The circulation rate was found to influence the degree of ASR conversion, most likely by altering the residence time of the ASR in the FR. Changes in conversion and carbon distribution during variation of the ASR feeding rate could not be attributed to the feeding rate itself but were most likely consequences of changes in oxygen transport. The only change that was attributable to the feeding rate was a change in tar maturation, due to the affected residence time of the gas. Finally, changes in the FR temperature had by far the strongest impact on tar maturation, although they had little effect on the carbon distribution between the various fractions, and variations in the other parameters meant that these changes could not be attributed solely to changes in the temperature.

#### 5.2.2.3. The relationships between oxygen transport, circulation rate, and fuel feeding rate

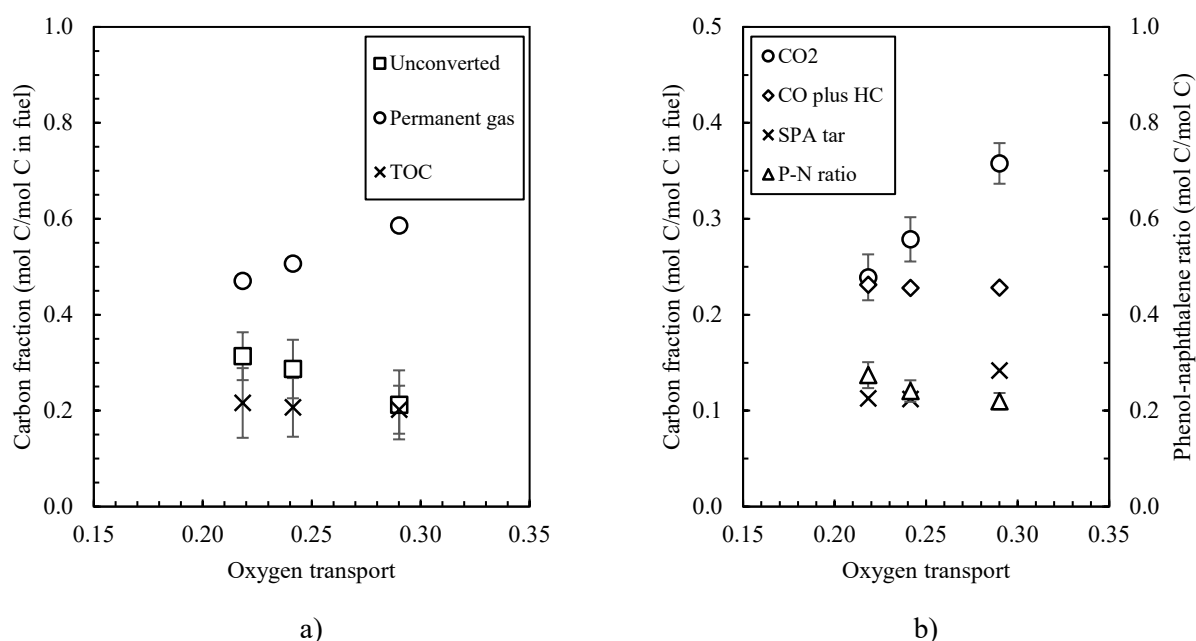
As discussed in *Section 5.1*, oxygen transport is linked to the circulation rate and the fuel feeding rate. The first linkage is a direct one: as the circulation rate increases, the rate of transfer of oxygen to the FR, in terms of moles of oxygen per unit time, increases. The second linkage is an indirect one: the oxygen transport is best expressed as the ratio of oxygen transported to the stoichiometric requirement

for complete oxidation of the fuel. This means that an increase in the fuel feeding rate decreases the level of oxygen transport.

However, as shown in Table 6, the experimental data-points compared for the purpose of measuring the effect of oxygen transport have similar circulation and fuel feeding rates. Therefore, the difference in oxygen transport must be due to other factors. These factors may include: better gas-bed material contacts, allowing for more reactions; a change in bed composition that enhances the reaction rates; and a change in particle structure that increases the reaction surface area. This may seem to be at odds with the previous claim that a near-steady-state situation was reached regarding the bed composition for the measurement points presented in this thesis. Nonetheless, the variation in oxygen transport cannot be attributed to a change in composition because a trend would have been observed over time. The reasons for the variation were not investigated in **Paper II** and, therefore, a specific phenomenon cannot be implicated. Still, the fact that the highest level of oxygen transport for the whole campaign was measured after a weekend during which the bed was only exposed to an oxidative environment suggests changes in the chemical structure of the bed. The level of oxygen transport decreased rapidly after a few hours in the alternating oxidative-reductive cycle, indicating that the changes faded away.

#### 5.2.2.4. Impact of oxygen transport on ASR conversion

The impacts of oxygen transport on the distribution of carbon into unconverted carbon leaving the FR, permanent gas, and TOC are shown in Figure 23a. The distributions of the carbon in the products, as CO and light hydrocarbons (referred to as “CO plus HC”), and as SPA tar, as well as the carbon in the form of CO<sub>2</sub>, are shown in Figure 23b. The ratio of carbon in the form of phenol to that in the form of naphthalene is also shown, as an indicator of tar maturation.



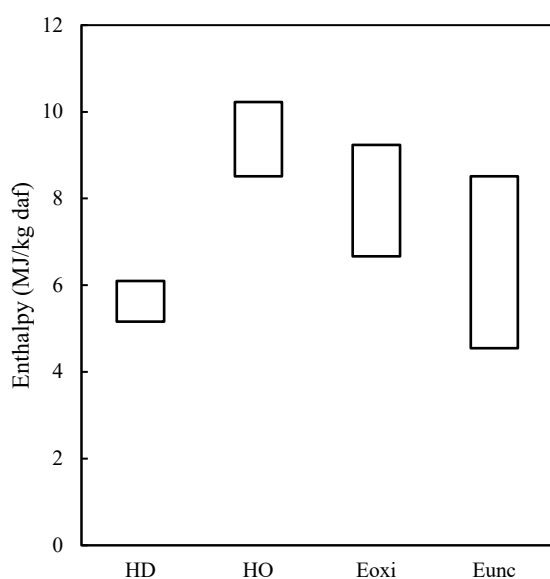
**Figure 23a.** Impact of oxygen transport on the distribution of carbon into permanent gas, TOC, and the unconverted fuel leaving the FR. The vertical error bars show the standard deviation for the carbon fraction. An explanation of how this standard deviation was estimated is provided in **Paper I**.

**Figure 23b.** Impact of oxygen transport on the distribution of carbon into CO<sub>2</sub>, CO plus HC, SPA tar, and the phenol-naphthalene ratio. The vertical error bars show the standard deviation for the carbon fraction. An explanation of how this standard deviation was estimated is provided in **Paper I**.

From Figure 23a and Figure 23b, it is clear that the oxygen transport increases ASR conversion, and that the carbon is converted exclusively to CO<sub>2</sub>. The TOC fraction is left unchanged, as is the SPA tar maturation. The carbon in the SPA tar is only slightly affected, but the last data-point is most likely an outlier, as a change in oxygen transport is not expected to cause changes in the SPA tar fraction. However, this outlier was obtained after a weekend under oxidizing conditions, as mentioned in *Section 5.2.2.3*. Therefore, this change could be attributed to the above-suggested mineral structure changes. Alternatively, the effect is due to the accumulation of catalytic species under oxidative conditions, for instance, from the constant biomass ash input in the combustor of the Chalmers DFB system. These catalytic species could then be released under reductive conditions. That the amount of carbon in SPA tar increases in the presence of these species is consistent with the observation that increasing the FR temperature also leads to an increase in the amount of carbon in SPA tar. This indicates that an increased process severity in the FR converts organic compounds that lie outside the measurement range to SPA-measurable tar.

#### 5.2.2.5. Heat balance closure

The heat balance of the DFB system was determined for the 14 experimental cases. The heat demand of the FR and the heat output of the associated AR are shown in Figure 24. The contributions to the heat output of the AR of the two heat production mechanisms, namely the oxidation of the bed material and the combustion of unconverted fuel from the FR, are shown in the figure as  $E_{\text{oxi}}$  and  $E_{\text{unc}}$ , respectively.



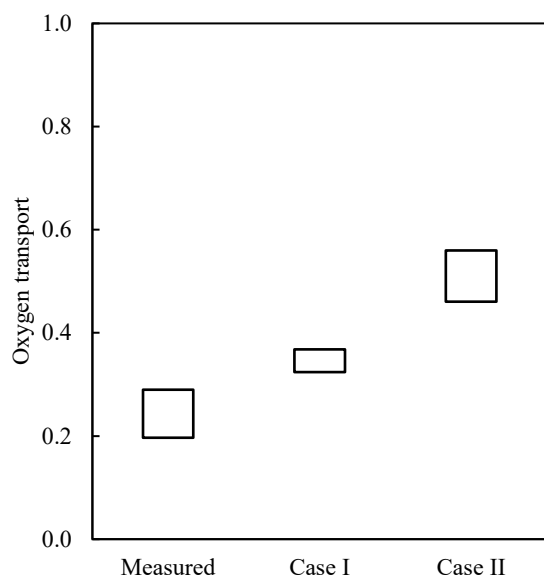
**Figure 24.** Ranges of values for the heat demand (HD) of the fuel reactor, the heat output (HO) of the combustor, the heat of oxidation of the bed material ( $E_{\text{oxi}}$ ), and the lower heating value of the unconverted fuel leaving the FR and entering the AR ( $E_{\text{unc}}$ ).

Figure 24 shows that, for all the cases examined, the heat demand of the FR can be covered by the heat output of the AR. Therefore, the DFB system can be operated using the operating conditions and fuel conversion parameters investigated in this work. The range of values for the heat demand and, to a lesser extent, for the heat output are narrower than the heat released from oxidation of the bed and of the ASR. This indicates that, despite the variability in the conditions covered, the heat balance is rather insensitive to these changes. Moreover, the differences in the heat demand and heat output are such that ASR conversion in the FR can be improved without altering the fulfillment of the heat demand.

Moreover, the heat produced from the oxidation of the bed material is comparable, and in most cases higher, than the heating value of the ASR leaving the FR. This suggests that operation in CLG mode is feasible, provided that the level of oxygen transport is increased.

It is, therefore, of interest to estimate the oxygen transport levels that would be required to operate the DFB system in CLG mode. This, of course, requires that the ASR is fully converted in the FR. Estimation of the heat demand associated with such a case requires, in turn, that the raw gas composition in such a case is known. The raw gas composition depends on the composition of otherwise unconverted ASR and on how the reactions in the FR would be affected by the products added from conversion of that ASR. As neither of these factors is known, it was assumed that the unconverted ASR was exclusively carbon and that its conversion produced only syngas, thus maximizing the energy penalty associated with it. The oxygen transport level required to operate in CLG mode was determined by increasing the level of oxygen transport until the heat output of the combustor was equal to the heat demand of the gasifier. All the added oxygen to the FR was assumed to react only with the syngas produced from the ASR conversion. The range of oxygen transport levels for all 14 experimental cases obtained from this extrapolation method is shown in Figure 25 as Case I.

Nonetheless, this extrapolation assumes that complete conversion is achieved without concern for how this might be achieved. Given that the oxygen transport was found to be the most impactful parameter with regard to ASR conversion, a second extrapolation was made, based instead on determining the oxygen transport level needed to convert fully the ASR. This was done by assuming that all the carbon from the converting ASR reacts with the transported oxygen to form  $\text{CO}_2$ . This is analogous to assuming that the ASR converts to syngas and is immediately oxidized by transported oxygen. This extrapolation is referred to as Case II in Figure 25.



**Figure 25.** Estimation of the oxygen transport levels required for two extrapolated cases, as compared with the range of oxygen transport levels measured. Case I corresponds to an extrapolation to complete carbon conversion in the fuel reactor and increasing the heat of oxidation of the bed via oxygen transport until the heat demand of the fuel reactor is equal to the heat output of the air reactor. Case II corresponds to an extrapolation to the level of oxygen transport required to convert fully the fuel, whereby the unconverted carbon becomes  $\text{CO}_2$ .

From Figure 25, it is apparent that levels of oxygen transport higher than those measured in this work are required to convert ASR in CLG mode. Based on the values obtained for Case II, achieving complete conversion solely by increasing the oxygen transport would require a significant increase in the oxygen transport level. The simplest way to increase the oxygen transport is to increase the bed-to-fuel ratio. However, a higher circulation rate reduces the residence time of the fuel, which is detrimental to the intended goal. Still, the viability of CLG lies in its ability to achieve near-complete conversion in the FR. The use of a carbon stripper would be necessary, regardless of the improvements made in ASR conversion in the FR, as achieving complete conversion without one is not realistic. Nevertheless, strategies to improve the rate of conversion are needed, to reduce the demand on the carbon stripper and thereby improve its efficiency.

Among the various potential strategies, the most promising way to improve significantly the conversion rate would be to reduce further the size of the pellets, given the large ASR pellet size used in this work. Increasing the temperature would likely improve the gasification rates, provided that complete devolatilization of ASR could be ensured in the FR. It should be noted that temperature was not found to improve the conversion rate in **Paper II**, although it is likely that the temperature range investigated was too narrow to see an effect, and that the devolatilization of the pellets was too limited to have a marked impact. Nevertheless, the impact of increased temperature on the organic fraction should be investigated. Indeed, the formation of heavy tar is to be expected at high temperature, as is the formation of soot. Besides, more than half of the carbon in the TOC could not be identified, which means that the composition of the TOC and its behavior at higher temperatures cannot be predicted. Finally, catalysts, such as AAEM, can be used to enhance char gasification rates. However, the interaction of the catalyst with the ASR-ash-rich bed needs to be determined.

The degree of conversion of the fuel can also be increased by reducing the fuel residence *via* the fuel mixing in the bed. As mentioned in *Section 1.2.3*, based on the work of Lundberg [53], the dominant mixing regime depends on the scale of the unit, so there is no one solution that is suitable for all cases. The fluidization velocity should also be carefully selected, as an increase in this parameter enhances the fuel lateral dispersion and the proportion of the fuel that follows the velocity field of the bed material, both of which lead to a decrease in residence time [53]. Furthermore, as suggested in *Section 5.1.2*, the shape and dimensions of the FR can be optimized to ensure simultaneously long residence times and high circulation rates. Given the degree of conversion desired, the introduction of baffles into CLG FRs will likely be a necessity.

Assuming that complete conversion can be achieved, reaching the required oxygen transport level remains a challenge, particularly if a higher level of oxygen transport is needed as part of the aforementioned strategies. The oxygen-carrying capacity of the bed may be the limiting factor in ensuring high oxygen levels of transport. This capacity can be improved by increasing the fraction of the oxygen-carrying phase in the bed, for instance, through magnetic separation of the iron-rich particles, which are likely to be the main contributors to the oxygen transport for the ASR-ash-rich bed. Nonetheless, the presence of aged (i.e., layered) olivine and the significant calcium content of the ASR-ash means that calcium sulfate-sulfide cycles may represent the other main contributor, such that their removal by magnetic separation becomes detrimental. The oxygen-carrying capacity of the bed could be increased by adjusting the ASR-ash composition during the production of said ASR by, for example, the addition of metal scraps. Thus, the oxygen-carrying bed formed by the accumulation of ASR-ash can, to a certain extent, be tailored.

### 5.3. Challenges associated with CLG

There are significant differences between the two main cases investigated in **Paper A** and **Paper II**. The composition of the fuel, from the viewpoints of the elemental composition and chemical structure, is linked to differences in behavior during conversion in the FR. Moreover, the compositions of the beds listed in **Paper A** were known, whereas in **Paper II** they could only be inferred. It is clear, when comparing Figure 23a and Figure 23b on the one hand, with Figure 19 and Figure 20 on the other hand, that the amount of CO<sub>2</sub> produced in the raw gas is higher in the wood pellets cases. This is attributed mainly to the comparatively higher oxygen content of the fuel and oxygen transport levels. The amounts of TOC and unconverted fuel produced with ASR are much higher than when wood is converted. Despite these differences, similar conclusions can be drawn from the studies in **Paper A** and **Paper II** regarding the challenges faced by the CLG process.

The main conclusion is that oxygen uptake and transport to the FR govern the process. They play dual roles, in both ensuring closure of the heat balance and enhancing fuel conversion in the FR. However, the latter role inevitably entails carbon oxidation to CO<sub>2</sub> in the FR, such that the CO<sub>2</sub> in the raw gas becomes the main carbon stream produced by the system. This makes the goal of operating in CLG mode and recovering most of the carbon in products paradoxical. As shown in Figure 17, neither diluting with an inert material nor reducing the bed-to-fuel ratio is a successful strategy for improving the CGE (which partly means increasing the carbon recovery in the products). Indeed, the opposite was the case: no effects were seen on the CGE, whereas the degree of char conversion dropped dramatically.

Of course, many of these issues are exacerbated by the fact that the Chalmers DFB system is not designed to operate in CLG mode. Nevertheless, the core issue remains that the transported oxygen is always be more likely to react with H<sub>2</sub> and CO, owing to the sizes of the molecules and their prevalences in the gas environment. The transported oxygen causes a transfer of carbon from the products to CO<sub>2</sub> in the raw gas, instead of contributing to the reforming of heavy hydrocarbons. Regardless of the optimization of the design of the CLG system or of the conversion process in the FR, CO<sub>2</sub> will be a major, and most likely the main, output of the process. This means that CLG makes sense when carbon sequestration is the main objective, whereas the production of carbon-containing products should be a secondary goal. In the case of CLG of biomass, negative emissions is a suitable goal, and the non-CO<sub>2</sub> side-stream could be used for the production of carbon-neutral products, heat, or power. However, in this application, CLG competes with DFB gasification with oxyfuel combustion. The choice of the most suitable technology will depend on the cost comparison between the amine scrubbing and subsequent CO<sub>2</sub> desorption on the one hand, and production of pure oxygen on the other hand. If production of an energy-rich, carbon-rich gas is the aim, CLG is likely not the technology to be preferred.

It is interesting to consider that, while this comes down to a choice of process for the case of DFB gasification of biomass, CLG is the only possibility when considering the gasification of ASR in a DFB. This is because of the cost associated with ensuring sufficient bed replacement to minimize the oxygen-carrying capacity. Similar to ASR, other rest fractions from extensive sorting processes that contain large amounts of metals would likely be suitable as feeds for thermochemical recycling by CLG. Therefore, even if CLG does not find a niche in biomass waste processing, it is worth studying for its role in ASR-like waste recycling.

If a sufficiently high value is assigned to sequestering carbon such that the carbon is deemed more valuable when it is in CO<sub>2</sub> than in products, then CLC appears to be a more viable approach. Indeed,

almost all the carbon can then be recovered and sequestered. Furthermore, despite all its associated issues, CLC does not suffer from the need to achieve a difficult balance in terms of oxygen transport and quality of products, since oxygen transport can be maximized without any concern.

Both CLG and CLC suffer, however, from the same conversion issue: some carbon will inevitably slip from the FR to the AR. Besides, coking of the oxygen carrier can occur, the regeneration of which entails carbon release in the AR. Moreover, it is likely that part of the products from the FR in CLG and CLC will not be considered as valuable (none of them will in the case of CLC) and will need to be destroyed in the AR. Finally, the carbon content in the FR fly ash needs to be recovered. As a consequence, the combustion of carbon in the AR is unavoidable. Thus, some carbon will be released to the atmosphere. Whether this amount is considered negligible or not will depend on the criteria established by Society in terms of CO<sub>2</sub> emissions and carbon recovery. It may then be necessary to use oxygen instead of air in the AR, which would produce a CO<sub>2</sub> stream that would need little cleaning in order to be sequestered. This would allow for more flexibility in terms of the degree of conversion in the FR, and would reduce the footprint of the AR. However, the value of this approach compared with simple oxy-combustion of the fuel combined with CCS needs to be assessed.

An important consideration is that the separation of the CO<sub>2</sub> will likely be highly energy-intensive. Indeed, the recovery of CO<sub>2</sub> from an amine scrubbing agent, which is the dominant technology for CO<sub>2</sub> separation, is an energy-intensive step: it corresponds to about 2–4 MW/kg CO<sub>2</sub> [92]. This issue will arise not only with CLG, but also when very active beds are used in DFB gasification. The energy cost must be accounted for when evaluating the overall energy efficiency of the CLG technology and, more importantly, the potential carbon stream associated with covering this heat demand must be carefully tracked and taken into account.

The many issues raised in this thesis indicate that the precise role and capability of CLG as a DFB technology for carbon recovery are currently unclear. Whether one considers carbon recovery in the form of products or in CO<sub>2</sub> for sequestration, there are other, better-suited options. Optimizing the CLG process remains a challenge, as conflicting aspects must be balanced. In summary, more work is needed to answer the question: “What will be the role of CLG in the future carbon cycle?”

# Conclusions

Dual fluidized bed-based gasification technologies have features that make them suitable for the future circular economy. As described in Chapter 1, the separation of the heat generation and the gasification reactions into two reactors with distinct gas atmospheres, combined with the possibility to use in-bed catalysts, opens the possibility to fine-tune the distribution of carbon into different fractions. The DFB process can be designed and optimized to maximize carbon recovery in the form of chemical precursors for downstream synthesis. CO<sub>2</sub> can be one such precursor, provided that it is separated and reacted with, for instance, hydrogen from a water-electrolysis plant. Conversely, CO<sub>2</sub> can be sequestered, which, if part of the carbon is sourced from biomass, contributes to negative emissions. Furthermore, as described in Chapter 2, DFB processes are especially well-suited to the incorporation of waste materials into the process at various levels. These materials can be used as additives to enhance the process or even as the centerpiece compounds around which the entire process is designed and optimized.

This thesis investigates how a DFB gasification system's carbon recovery can be optimized by taking advantage of the properties of waste materials. Two aspects were investigated. The first aspect was the use of a waste that is inherent to the process, i.e., flue gas coarse ash, to improve the activity towards tar abatement and, thereby, increase carbon recovery as valuable products. The second aspect was investigated in two experimental campaigns using two different waste-derived bed materials, one of which was produced internally by the fuel ash, to operate the process as a CLG unit. The carbon distribution from the CLG process and its feasibility were assessed.

The main outcomes of this thesis are that:

- Increasing the activity of the bed material results in substantial transfer of carbon from the products to CO<sub>2</sub> in the raw gas, as expected from the intensification of the WGS reaction. This indicates that achieving a high level of activity so to generate as little tar as possible and the desired H<sub>2</sub>/CO ratio should not be the ultimate goal of DFB gasification processes, and that the fate of CO<sub>2</sub> should be carefully considered.
- The activation rate and activity level of the bed material with regard to tar reforming and cracking reactions can be enhanced by circulating coarse flue gas ash back to the DFB. From the standpoint of tar abatement, DFB processes should be designed to allow continuous operation of the external material loops formed by the circulation of flue gas and gasification ash.
- CLG of both woody biomass and ASR leads to a carbon distribution that is dominated by CO<sub>2</sub> in the raw gas. The inevitable combustion in the FR of valuable gases, in particular H<sub>2</sub> and CO, leads to a low CGE, as a significant portion of the fuel's energy content is expended to chemically reduce the oxygen carrier in the FR.
- CLG could of interest when simultaneous production of chemical precursors and sequestration of carbon is desired. However, CLG competes in this application with DFB gasification with oxy-combustion. Choosing the most suitable technology should be based on a cost comparison of amine scrubbing and the production of pure oxygen.
- If either the production of chemical precursors or carbon sequestration is considered separately, other DFB processes appear to be more suitable than CLG, e.g., regular DFB gasification or in combination with electrification to create carbon products and CLC for carbon sequestration.
- In the case of a metal-ash-rich waste such as ASR, CLG becomes the inevitable conversion route in a DFB gasification system. In that case, strategies to increase the oxygen transport are

needed to avoid dependence on the combustion of part of the process products or additional fuel. Increasing the oxygen transport will likely be achieved by a combination of: careful process optimization, fuel preparation, and the tailoring of the fuel-ash composition during its production.

## Recommendations for future work

In this thesis, several ways to manage the carbon recovery from DFB gasification systems have been discussed, and two have been investigated: (i) increasing carbon recovery as valuable products by increasing the catalytic activity of the bed; and (ii) CLG of biomass and ASR. CLG faces some challenges that make its potential role as a carbon-extracting technology unclear. The next step is, therefore, to establish the circumstances in which the CLG technology is more suitable than the alternatives, in particular oxyfuel-based DFB gasification.

The characteristics of the other processes discussed in Chapter 1 should be investigated, in terms of their carbon recovery, operational feasibility, and energy balance, among other factors. The interactions of these processes with the energy system, the carbon cycle, and the environment must be included in these analyses. Furthermore, the incorporation of waste materials into the processes should be explored, in line with the concepts of the circular economy and so as to take advantage of the properties of these waste materials. The possibilities to valorize waste from the DFB process, through extracting and recycling ash components, must also be evaluated.

Finally, among the waste materials that could be incorporated into the processes, a strong emphasis should be placed on those that contain carbon and those that will be the future carbon sources of the circular economy. Their characteristics and behaviors in the various DFB processes should be explored, so as to identify opportunities for efficient recovery of their carbon.

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