

1 Introduction

1.1 Motivation

The continuous utilization of fossil energy resources and the related emissions of greenhouse gases (GHG) represents a major threat to humankind. The current scientific consensus is that the increase of GHG concentration in the atmosphere leads to a rise in the global-mean temperature on earth [1, 2]. Several challenging consequences such as a growing number of extreme weather events or the rise of seawater level are related to this phenomenon. Among the contribution of the GHG, such as methane (CH_4), water vapor (H_2O), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6), carbon dioxide (CO_2) represents the major share [3].

As shown in Figure 1-1, there is a remarkable increase of the global average CO_2 concentration in the atmosphere, which is directly linked to the start of the industrial activities in the beginning of the 18th century. By the year 2017, a global average CO_2 concentration of more than 400 ppm_v has been reached. This represents an increase of almost 50 % in comparison to the pre-industrial value of approximately 280 ppm_v . The rise of the CO_2 concentration is mainly caused by the extensive utilization of fossil-carbon based primary energy carriers, such as coal, oil or natural gas. These substances are typically combusted to generate heat, which is either directly used or further converted into other forms of energy, such as electricity. Nowadays, fossil fuels still represent the dominating primary energy carrier in almost all fields of relevant activities such as power generation, industry, transportation or building (i.e. heating) [4].

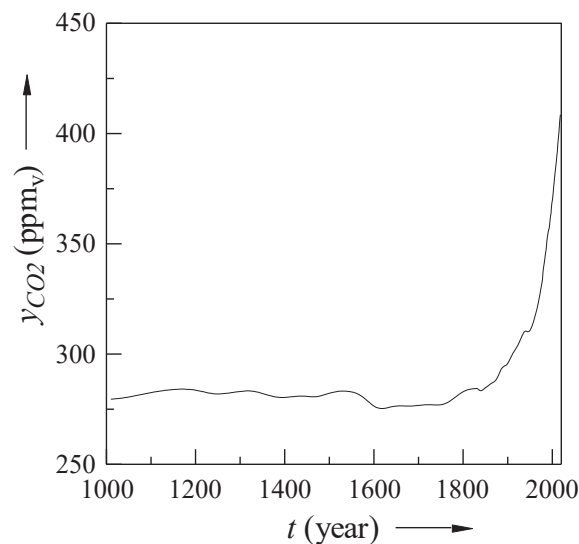


Figure 1-1: CO_2 concentration in the atmosphere from the year 1000 to 2017, data from [5, 6].

According to a data set from the International Energy Agency (IEA) [7], the global CO_2 emissions related to the combustion of fossil fuels accumulate to approximately 32.8 Gt_{CO_2} in 2017. This number represents the highest value ever noticed. The power and heat generation sector thus represents the major emitter with a total emitted amount of approximately 13.5 $\text{Gt}_{\text{CO}_2}/\text{a}$, followed by



the sectors of transportation (8.0 Gt_{CO2}/a) and industry (6.2 Gt_{CO2}/a). Amongst the latter, energy-intensive industries such as steel- or clinker-making processes account for yearly CO₂ emissions of almost 1.7 Gt_{CO2}.

In order to limit the effects of climate change to an acceptable level, a drastic reduction of further GHG emissions is required. At the Paris Conference of the Parties (COP) 21 in 2015, the 195 nations agreed on the target to limit the increase of global-mean temperature to not more than 2 °C (preferably below 1.5 °C) in comparison to pre-industrial levels (1850 - 1900) [8]. For the energy sector, this implies changes in the way of energy supply, utilization and conversion. Additionally, new technologies need to be developed for an implementation in the long-term perspective.

In Figure 1-2, two energy technology perspectives proposed by the IEA from the years 2020 to 2060 are presented. Graph a) shows the “2 °C Scenario” (2CS), aiming on a CO₂ emission reduction, adequate for limit the rise of global-mean temperature at 2 °C compared to pre-industrial levels. Graph b) shows the “Beyond 2 °C Scenario” (B2CS), which aspires to a limit of the global-mean temperature rise at 1.5 °C compared to pre-industrial levels.

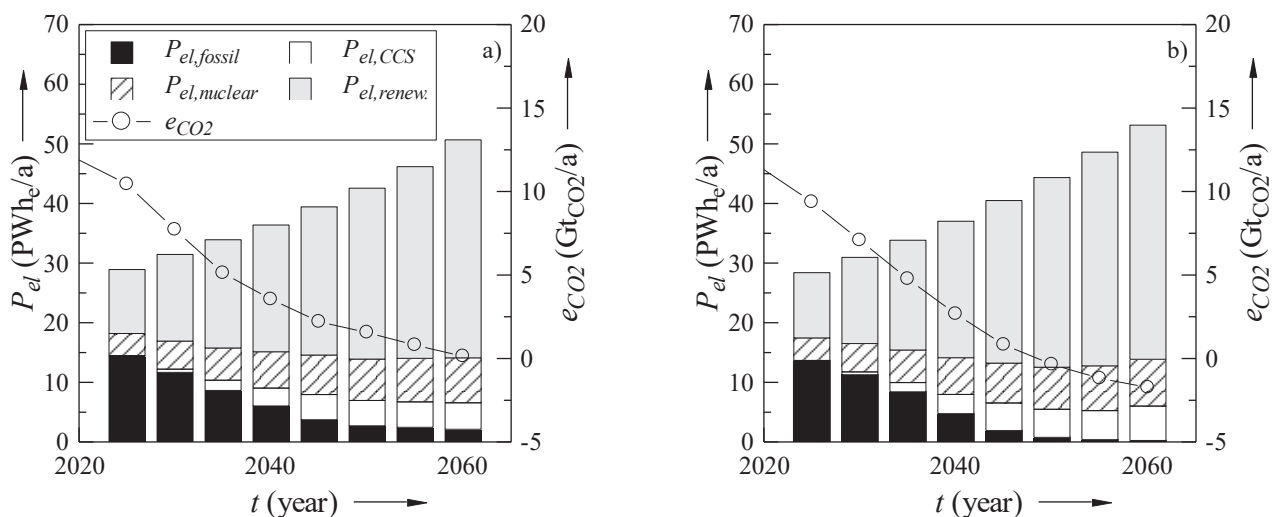


Figure 1-2: Energy technology perspective scenarios for the energy sector. 2 °C scenario (a) and beyond 2 °C scenario (b), data from [9].

Both scenarios are based on a large-scale implementation of renewable energy sources. In the year 2060, more than 70 % of the global power demand is supplied by technologies that rely on primary energy in the form of wind, solar radiation or hydropower. Furthermore, nuclear energy plays a key role for achieving the desired CO₂ emission reduction goal in each scenario. As a third measure, the application of carbon capture and storage (CCS) processes is foreseen for the second half of the century. In the 2CS, approximately 4,400 TWh_e are supplied by CCS equipped power systems. In the B2CS, this number is forecasted to almost 5,800 TWh_e. Putting these numbers into perspective, it requires approximately 660 or 870 CCS equipped full-scale state-of-the-art power plants in 2060 for the 2CS and for the B2CS, respectively.

As a consequence of the proposed power generation infrastructure, the related CO₂ emissions decrease considerably. In the 2CS, the yearly CO₂ emissions decrease significantly in the first half of the century, whereas a moderate reduction is foreseen after 2045. This leads to CO₂ emissions due to the power generation sector of approximately 0.13 Gt_{CO2}/a in 2060. The reduction pathway is even more ambitious in the B2CS, where CO₂ emissions of -1.74 Gt_{CO2}/a are expected for the year 2060. Thus, CO₂ is removed from the atmosphere, while power is produced. Atmospheric CO₂ removal in



the framework of power generation systems is feasible due to the utilization of biomass-based fuels in combination with CCS equipped power plants. Accordingly, the power generation in CCS equipped, biomass-fueled power plants accounts for approximately 2,214 TWh_e/a in the B2CS.

1.2 Objectives of the Thesis

Globally, there will be an increasing capacity of wastes that need to be handled in the future. According to the current technological knowledge, thermal waste treatment is seen as the most promising technology to be applied in this regard. As a consequence, Waste-to-Energy (WtE) plants will remain a relatively large CO₂ point emitter even in the long-term. In addition to that, there is the need to achieve negative CO₂ emissions in order to limit or even to reduce the CO₂ concentration in the atmosphere. Taking into account the organic waste fractions in Municipal solid waste (MSW), CCS equipped WtE plants could be applied to contribute to an achievement of both aforementioned needs. MSW is thereby treated in an environmentally friendly way, while heat and/or power, as well as negative CO₂ emissions, are supplied.

The carbonate or calcium (CaL) process represents an appropriate method for post-combustion CO₂ capture from newly built or already existing WtE plants. In this process, the capture of CO₂ from a flue gas stream is achieved by the cyclic carbonation-calcination of a circulating sorbent in two interconnected fluidized bed reactors, namely carbonator and calciner. The required heat to run the process is supplied by the combustion of supplementary fuels in the calciner. The feasibility of the process has already been experimentally demonstrated up to megawatt-scale using hard coal, lignite or natural gas as supplementary fuels. The CaL process is particularly suited for being retrofitted to existing plants. Among the processes for CO₂ that are currently researched, the CaL process shows a relatively low efficiency drop along with moderate CO₂ avoidance costs in the framework of a coal-fired power plant. Its application under the conditions of a WtE plant has neither experimentally nor techno-economically investigated yet. In such an arrangement, waste-derived fuels could be applied to heat the process. In contrast to the utilization of fossil-fuels, this implies low or even negative fuel costs, an improved carbon balance and a higher total waste throughput of the retrofitted WtE plant.

This thesis will classify the atmospheric CO₂ removal by means of CaL process-equipped WtE plants among other competitive technologies. A two-stage evaluation will be applied. First, an extensive experimental investigation of the CaL process under the boundary conditions given by the desired application is carried out at a 1 MW_{th} CaL pilot plant. This particularly implies for the first time worldwide the utilization of solid recovered fuel (SRF) in the calciner of the CaL process and the decarbonization of a flue gas similarly to that of a typical WtE plant fueled by MSW. Due to the strong influence of fuel properties on the CaL process performance, it is crucial to ensure the ability of the sorbent to absorb CO₂ by means of long-term investigations.

Based on a detailed experimental investigation, a comprehensive techno-economic assessment of the application of the CaL process for post-combustion CO₂ capture in the field of WtE plants is carried out. For the appropriate calculation of heat and mass balances, the CaL process model is validated by experimental data. The thermodynamic assessment covers a wide range of process conditions and possibilities for excess heat utilization. The economic calculations rely on a bottom-up approach for the investment costs of relevant components. In order to compare the techno-economic process performance among other technologies for atmospheric CO₂ removal, economical extreme scenarios are evaluated.



1.3 Thesis Outline

This thesis is structured as follows.

In Chapter 1, the challenges of modern society related to the extensive emission of GHG are described. Based on a general overview of climate change mechanisms, the need for negative CO₂ emissions is substantiated. Finally the objectives of this thesis and its structure are derived.

Chapter 2 provides the theoretical fundamentals that are associated with this thesis. This includes an overview of the global waste generation and the treatment of wastes in WtE plants. Thereafter, technical possibilities for climate change mitigation by means of CCS processes are provided. Each step of the CCS process chain is explained and discussed, in addition to the presentation of suitable processes that allow for negative CO₂ emissions. Based on the fundamentals of fluidization engineering and fluidized bed combustion, a state-of-the-art review of CaL process technology is presented. Particular attention is given to the carbonation-calcination reaction, sorbent deactivation mechanisms and existing experimental CaL process test facilities, as well as the techno-economic performance of the CaL process.

Chapter 3 focuses on the experimental investigations at the 1 MW_{th} CaL pilot plant. Based on a simplified process flowsheet, the main components and auxiliary systems of the CaL pilot plant at Technische Universität Darmstadt are explained. This includes the measurement devices for pressure, temperature, volumetric flow rate and gas composition as well as the auxiliary systems of the pilot plant. Thereafter, the main results of two consecutive CaL test campaigns at the pilot plant are presented and discussed. The evaluation is based on simplified reactor models for carbonator and calciner which are typically applied in the field of CaL technology. In addition to the CO₂ capture performance of the CaL process, a comprehensive evaluation of gaseous emissions related to the combustion of SRF is carried out. The specific emissions of CO, NO, SO₂ and HCl are thereby compared among different combustion conditions, with particular focus on the oxyfuel combustion under conditions of the CaL calciner.

In Chapter 4, a detailed process model for the calculation of the CO₂ absorption efficiency and sorbent conversion in the CaL carbonator is applied. Based on experimental data from the 1 MW_{th} pilot plant, the model is further validated. A sensitivity study points out effects of crucial process parameters on the CO₂ absorption characteristics in the carbonator. The validated CaL process is then applied to the techno-economic analysis in Chapter 5.

Chapter 5 is comprised of the techno-economic investigations of a generic 60 MW_{th} WtE plant being retrofitted by the SRF-fueled CaL process. Based on the heat and mass balances delivered by the validated process model, key performance indicators such as levelized cost of electricity or cost of CO₂ avoidance are calculated by a bottom-up approach. As the CaL technology is still at an early stage of development, a comprehensive sensitivity study is carried out in terms of technical and economical parameter variations. Additionally, novel concepts for CaL process excess heat integration into the existing WtE plant due to external super- and re-heating are proposed and thermodynamically evaluated.

Finally, Chapter 6 summarizes the main results of this thesis. Conclusions are drawn from the research and major fields for further investigations are proposed and highlighted.



2 Current State of Research

This chapter covers the current state of research in the fields that are relevant for this thesis. In particular, an overview of the current waste management strategies, the waste treatment in dedicated WtE plants and the waste processing and upgrading towards SRF is given. Thereafter, the theory of CCS is explained for each particular process step. Based on the fundamentals of fluidization engineering, the main mechanisms of the gaseous pollutant formation and mitigation with regard to the fluidized bed combustion of solid waste-derived fuels is explained. Finally, the current state of knowledge related to the CaL process is introduced.

2.1 Waste Management

In the course of the following section, an overview of global waste generation is presented. Different strategies are available for the treatments of waste streams. Among others, the thermal treatment in WtE plants represents one suitable option. The unique characteristics of WtE plants are then further introduced and described. Finally, the processes relevant for upgrading raw wastes towards more classified fuels is illustrated using SRF as an example.

2.1.1 Global Municipal Waste Generation and Treatment Strategies

The global generation of MSW is directly related to the growth rate of the population and the associated industrial activities. Its generation is consequently expected to grow from nearly 1.3 billion tons per year currently, to approximately 4.0 billion tons per year in 2025 [10]. In the EU-28, approximately 239 million tons of MSW were generated in 2014, which means 475 kg_{MSW} per capita, or 23 kg_{MSW} per 1,000 EUR of gross domestic product [11].

MSW consist of a wide range of substances. Exemplarily, Figure 2-1 depicts the mass composition of MSW for a low- and for a high-income level country, respectively. The mass compositions is classified towards organics (e.g. wood, food residues), papers (e.g. newspaper, cardboards), plastics (e.g. packaging, bags), glasses (e.g. bottles, colored glass), metals (cans, foil), textiles and others (leather, rubber).

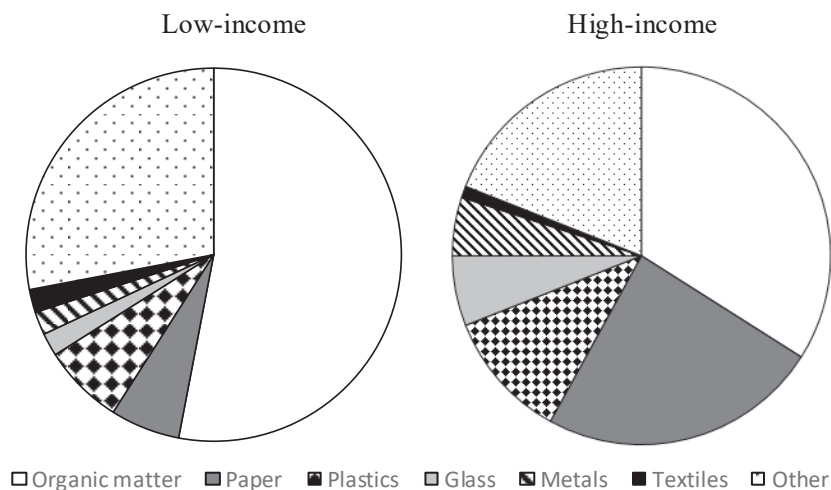


Figure 2-1: Composition of MSW dependent on the country income level, data from [12].



The composition of MSW strongly depends on the income level of the considered region/country. In a high-income country, the quantities of first-world waste products such as plastics, papers or glasses are higher in comparison to a low-income country. Contrary to that, the share of biogenic wastes is noticeably increased in regions with a low income level (34 % vs. 53 %).

Different methods are applied for the minimization and mitigation of wastes, which can be categorized according to the waste treatment hierarchy as shown in Figure 2-2. Accordingly, the approaches with the lowest environmental burden are classified at the top and should be preliminary applied. In the downward direction, the lifecycle impact of the waste treatment methods increase.

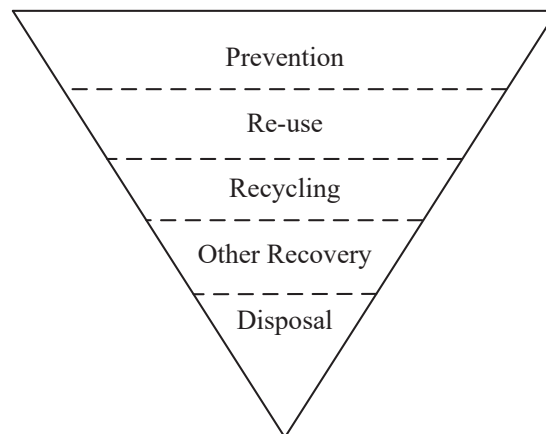


Figure 2-2: Waste treatment hierarchy, adopted from [13].

The prevention of waste represents the ideal approach, as neither resources are utilized to generate a certain product, nor does the product need to be treated after its original purpose. Re-use is favorable to recycling, as the recycling step implies a process for the chemical or physical conversion of the old into the new product. One example is the direct re-use of packing material (e.g. bottle, box) instead of the recycling of the old plastic material to a new product. Other waste recovery approaches include thermal recovery by means of combustion processes or the chemical recovery by means of synthesis gas utilization via a gasification process step. The least desirable option is the disposal of wastes, as no further product or service is recovered from the waste substance after its desired utilization.

The currently applied strategies for the treatment of wastes that are neither applicable to recycling nor to re-use include the uncontrolled waste dumping, the landfilling of wastes with or without landfill gas collection and the incineration in WtE plants. In high-income countries, the thermal treatment of wastes or its controlled landfilling is mostly applied, while on the other hand low-income countries still dispose their wastes in uncontrolled dump sites [10]. In the EU, on an average basis 28 % of MSW are recycled, 27 % incinerated, 16 % composted and 28 % are landfilled [11].

In case of uncontrolled waste dumping, the emissions of methane as a consequence of the biological degradation processes significantly contribute to the global GHG emissions. According to a report from the U.S. Environmental Protection Agency, the methane emissions from uncontrolled landfills account for almost 12 % of global methane emissions [14]. Furthermore, the release and distribution of hazardous species such as heavy metals in the ecosystem is of major concern. Suitable waste treatment strategies are thus required in order to limit the pollution of the ecosystem and the emission of greenhouse gases because of inappropriate waste disposal now and in the future.



2.1.2 Solid Recovered Fuel

The term solid recovered fuel refers to a specially pre-treated type of waste-derived fuel, processed from production-specific wastes, non-hazardous industrial wastes or MSW [15]. It is the successor of the refuse derived fuel (RDF), which has come onto the market during the 1970s.

The main constituents of SRF are plastics, paper, cardboard, textiles and wood. Plastics could be in the form of thin foils or hard plastic structures in various 3D shapes. Wood might be derived from demolition wood or production residues. The major steps within an SRF processing plant include shredding, metal separation, sieving and size reduction. SRF is typically utilized in dedicated mono-combustion units, cement plants and as a substitute fuel in fossil-fired power and industrial plants [16-18]. The different fuel constituents have a considerable influence on the combustion properties of SRF. As the composition of SRF is highly dependent on countries, regions and seasons, a classification approach has been proposed by the EU [19]. The following key classification characteristics were introduced:

- Mean net calorific value, in MJ_{th}/kg (as received)
- Mean chlorine content, wt.% (dry)
- Median and 80th percentile mercury content, mg/MJ_{th} (as received)

Based on the above mentioned characteristics, five different SRF quality classes are distinguished according to Table 2-1. The diverse nature of SRF becomes apparent when taking into account the different net calorific values. While the net calorific value of Class 1 is comparable to the corresponding number of a typical hard coal, the energy content of Class 5 is almost insignificant.

Table 2-1: Classification characteristics and quality classes of solid recovered fuel [20].

Characteristic	Statistical measure	Classes				
		1	2	3	4	5
Net calorific value	Mean	≥ 25.0	≥ 20.0	≥ 15.0	≥ 10.0	≥ 3.00
Chlorine	Mean	≤ 0.20	≤ 0.60	≤ 1.00	≤ 1.50	≤ 3.00
	Median	≤ 0.02	≤ 0.03	≤ 0.08	≤ 0.15	≤ 0.50
Mercury	80 th percentile	≤ 0.04	≤ 0.06	≤ 0.16	≤ 0.30	≤ 1.00

In contrast to traditional fossil fuels such as coal, oil or natural gas, SRF offer the advantage of a moderate carbon footprint due to organic waste fractions. Furthermore, fuel prices are usually notably reduced in comparison to conventional fossil fuels. Depending on the regulatory framework and the waste-management system, even negative fuel prices are feasible [21]. In contrast, the requirements of the combustion system increase due to challenging fuel species contained in SRF. In this respect, chlorine poses the main threat because of the risk of high-temperature corrosion. In order to prevent boiler materials from exhausting corrosion rates, the temperature of the live steam is typically reduced (see Chapter 2.1.2). Another challenging aspect of SRF is the presence of coarse mineral matter and incombustible substances. Therefore, special attention needs to be paid to the design of the ash extraction systems of SRF-fueled combustion units.

Figure 2-3 gives a comparison of the specific CO₂ emissions (*e_{CO2}*) for different types of fuels referring to the total and fossil share of CO₂, respectively. For biomass a biogenic carbon fraction of 100 % is assumed, with 40, 45 and 65 % for SRF I, SRF II and MSW. In the case of the latter three fuel types, a variation in the biogenic carbon fraction of +/- 20 % is additionally indicated.

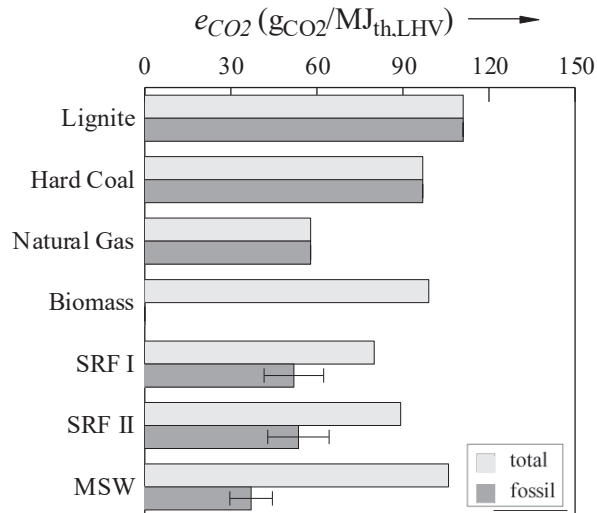


Figure 2-3: Comparison of the specific CO₂ emissions (e_{CO_2}) for different types of fuel, data from [22-24].

The total specific CO₂ emissions are least favorable in case of lignite (e_{CO_2} : 111 gCO₂/MJ_{th,LHV}) and MSW (e_{CO_2} : 106 gCO₂/MJ_{th,LHV}). On the other hand, natural gas allows for the lowest total specific CO₂ emissions (e_{CO_2} : 57.8 gCO₂/MJ_{th,LHV}). If only the share of fossil CO₂ is considered, the comparison shows a different characteristic. The utilization of pure biomass is considered as almost CO₂ neutral, which results in net zero CO₂ emissions. The second best option in this regard is MSW; its combustion leads to specific CO₂ emissions of 37.1 gCO₂/MJ_{th,LHV}, followed by the two types of SRF with approximately 52.8 gCO₂/MJ_{th,LHV}. Even though the large-scale combustion of pure biomass might not be fully harmonized with the planetary boundaries, the utilization of waste-derived fuels allows for a better specific CO₂ emissions balance than all other fossil fuels typically considered for power generation. Due to increasing share of biogenic feedstock in the chemical industry that is forecasted in the long-term, it is likely that the fossil-fraction in waste-derived fuels will decrease even further in the future.

2.1.3 Waste-to-Energy Plants

The incineration of raw MSW in WtE plants is a widely used waste treatment methodology. The main purpose of a WtE plant is the reduction of waste mass, volume and toxicity while generating power and/or heat by the utilization of the energy chemically bound in the MSW as a useful byproduct [25]. These days, nearly 28 % of the MSW capacity in the EU-28 is treated by means of incineration [26]. Worldwide, more than 750 WtE plants with a yearly MSW treatment capacity of almost 83 million tons are currently in operation [12].

The net electrical efficiency of a typical WtE plant ranges from 10 to 30 %. This relatively low value is caused by several reasons, such as the low energy content of the raw MSW, its fluctuation in composition and size as well as the various corrosive species contained in the MSW reducing the effectiveness of heat recovery. Combustion systems for MSW, such as moving grates or fluidized beds, are specifically designed to guarantee a stable plant operation, complete fuel burnout along with non-toxic emissions rather than aiming at maximum boiler efficiency. The power cycle of a WtE plant is exposed to multiple material demanding phenomena, such as high temperature corrosion, molten salt corrosion, fouling and the erosion of heat exchanger surfaces [27, 28]. In addition to the high temperature corrosion on boiler and superheater surfaces, there is also the risk of low-temperature corrosion [29]. To prevent the low-temperature corrosion at the outlet of boiler and in



the flue gas treatment path, the minimum temperature from exiting flue gas streams is limited, which again lowers the water-steam cycle efficiency. Furthermore, WtE plants are often applied for the delivery of heat as the main product, which raises the need for the application of the total energy efficiency rather than only taking into account the net electrical efficiency. Exemplarily, Figure 2-4 shows the energy flows of WtE plants delivering power only (a) and heat and power (b).

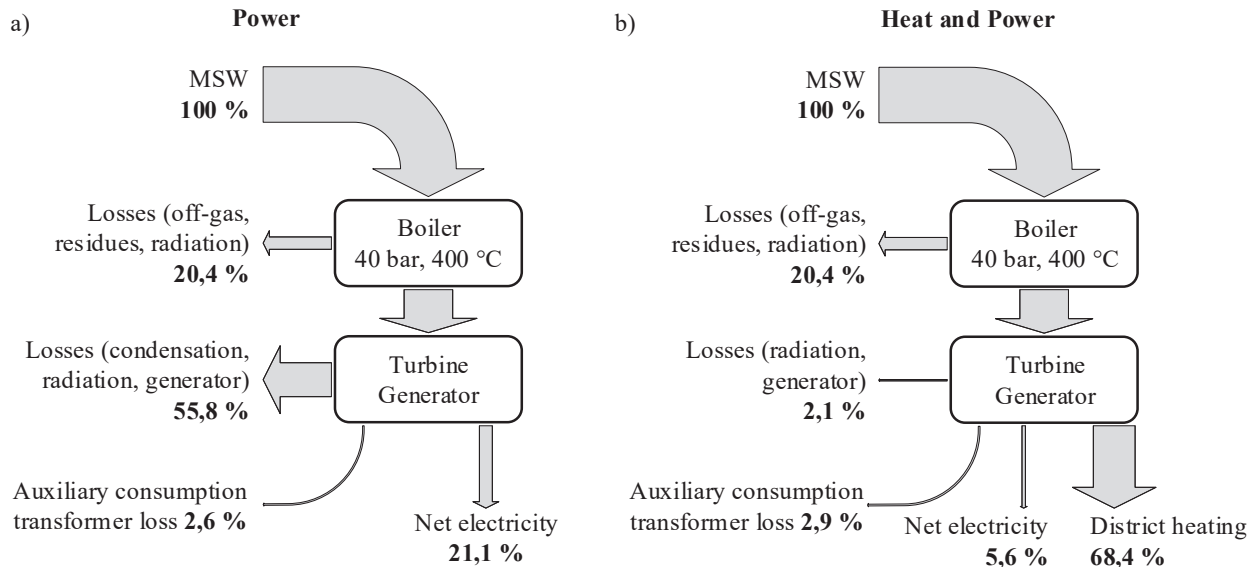


Figure 2-4: Energy flows in WtE plants that produce power (a) or heat and power (b), adopted from [30].

The parameters of the superheated steam at the turbine inlet are similar in both plants, while the total energy output differs significantly between both approaches. When producing heat and power, 74.4 % of the chemical energy in the MSW feed is converted into the desired product, whereas this number is reduced to 21.2 % in case of power as the only product. However, electricity output in the heat and power case is limited to 5.6 % of total energy input, while 68.4 % of total energy input is converted to hot water for district heating applications. Energy losses related to the condensation of steam at the turbine outlet are thus minimized in the heat and power case.

A WtE plant represents a highly case specific system that is tailored to fit the prevailing boundary conditions, such as local stack emission limits, fuel composition and the desired output product [31]. Especially the water-steam cycle layout varies among different applications. For example, Figure 2-5 shows the live steam parameters as a function of the gross electrical efficiency for WtE plants located in the EU.

In order to reduce the high temperature corrosion induced material losses to an acceptable value, the temperature of the superheated steam is often limited to approximately 400 °C [32]. For both types of WtE plants, the major share of the units thus operate at live steam parameters of 400 °C and 40 bar, leading to a gross electrical efficiency between 20 % and 30 %. As the extent of corrosion induced material losses is related to the chemical composition of the fuel and to the mitigation measure that are applicable under certain conditions, some of the WtE plants operate with a live steam temperature even above 500 °C and 75 bar. This results in an increased gross electrical efficiency of 30 - 35 %. Furthermore, the more diverse nature of heat and power producing WtE plants in terms of water-steam cycle layout becomes apparent when comparing both graphs.

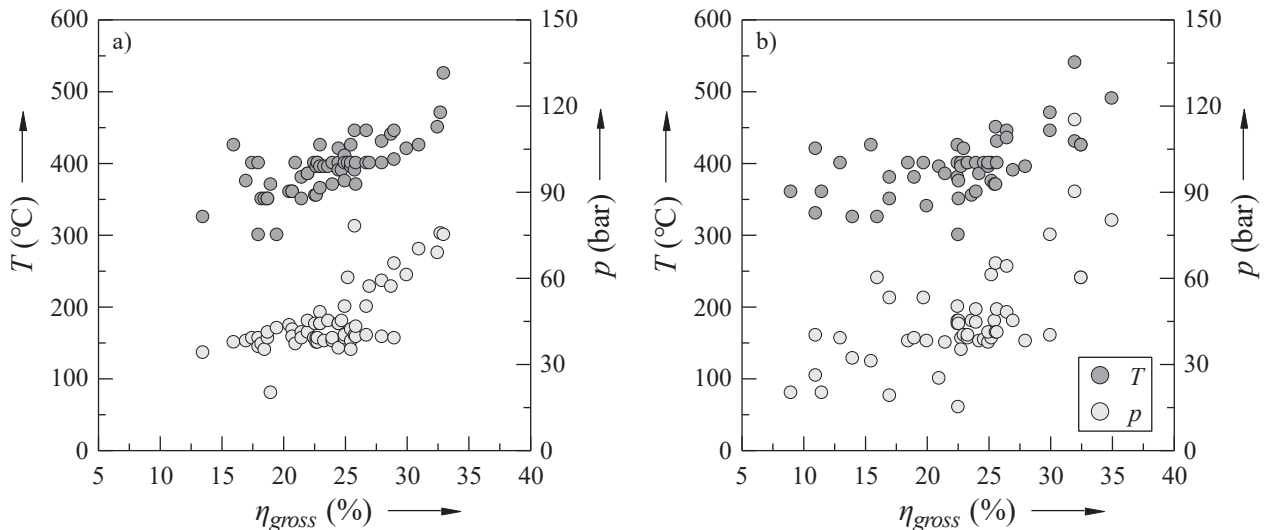


Figure 2-5: Gross electrical efficiencies (η_{gross}) for different live steam parameters (T , p) for WtE plants that produce power only (a) or heat and power (b), data from [33].

2.2 Carbon Capture and Storage

The capture of CO_2 from exhaust gases of large-scale point emitters and its subsequent long-term storage represents one option to reduce anthropogenic GHG emissions [34, 35]. A CCS system consists of processes for the capture of CO_2 , its purification, transportation and injection into an appropriate long-term storage reservoir.

Furthermore, the highly concentrated CO_2 is suitable to be utilized as raw material for chemical processes or synthetic fuel [36, 37]. Consequently, the process chain is called carbon capture and utilization (CCU). In the case of a CCU application, the long-term CO_2 avoidance potential highly depends on the type of product that is derived and from the quantity of fossil feedstock that is replaced by the captured carbon. For example, the conversion of CO_2 into a synthetic fuel, such as methane or methanol, inevitably leads to the re-release of CO_2 once the fuel is combusted. Thus, it is rather complex to determine the positive effect of CCU with regard to the long-term CO_2 emission mitigation potential. The framework of this study is limited to the assessment of CCS and the related long-term storage of CO_2 .

2.2.1 Capture

Within a CCS process chain, the process step of CO_2 capture represents the most energy and capital intense process step. Different approaches for CO_2 capture are distinguished according to the occurrence of the CO_2 capture process relatively to the stage of CO_2 formation (i.e. combustion). Figure 2-6 shows these three approaches for CO_2 capture applied to a process for the delivery of heat and/or power. The type of fuel might differ among coal, biomass, natural gas and waste or waste-derived fuels. Their common factor is the presence of carbon in the fuel which causes the formation and subsequent emission of CO_2 .

The pre-combustion approach involves the capture of CO_2 upstream of the combustion process. In the case of a solid fuel, the first process step comprises the gasification of the fuel in order to produce a syngas that contains mainly H_2 , CO and CO_2 . For gaseous fuels, the syngas is achieved by means of a reforming process. Thereafter, the syngas undergoes several cleaning and upgrading steps, such as CO-shift and CO_2 capture in order to achieve an almost pure H_2 -stream that is subsequently