Grate Furnace Combustion: 
A Model for the Solid Fuel Layer

PROEFSCHRIFT

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Preface

Biomass is a renewable source of energy which will probably play an important role in the transition towards a more sustainable energy supply. This thesis contains a study aimed at developing models to study the formation of NOx-emissions of biomass grate furnace combustion, an attractive conversion technique for medium and small scale energy supply for power generation and district heating. In this preface, the social, scientific and organizational context in which the study was performed will be described.

The study presented in this thesis offered me the opportunity to address the interests of different stakeholders that are involved in the global effort to make combustion processes cleaner, more efficient and more sustainable. For scientists, the results presented in this thesis lead to an improved understanding of solid fuel conversion and emission formation. For engineering companies, tools and results are described that can be used to meet the emissions regulations by optimizing the design and operating conditions of a plant. For operators of grate furnaces, such optimized furnaces lead to reduced costs of acquirement and operation, less emissions and increased fuel flexibility, to name a few examples. For society, wider application of biomass grate furnace conversion will lead to a better environment due to reduced emission of greenhouse gasses and pollutants and a more secure energy supply due to decreased demand for fossil fuels.

The present study offered me also the opportunity to work on an interesting scientific topic that involves different scientific disciplines. Different scientific disciplines are involved because a large number of phenomena take place in a biomass conversion process. Examples of these phenomena are the thermal decomposition of solid fuel particles, gas phase kinetics and heat and mass transport. The present study therefore involves elements from chemistry (heterogenous and homogenous reactions), physics (fluid dynamics) and mechanical engineering (reactor design). The main scientific field in which the current study is performed is the discipline of combustion science, which offered valuable research tools and concepts (1-D models, asymptotic methods, kinetic mechanisms, reactive flow solvers). In addition, the field of process technology is important for this study, because it considers grate furnace conversion as a process in which the output parameters (energy and emissions) can be optimized by adapting operating conditions, furnace design and fuel properties.

The organizational framework in which this study has been performed is the project “Optimization and Design of Biomass Combustion Systems”. This project was part of the Fifth Framework Programme of the European Union (Project number: NNE52001-00693). Partners were the Netherlands Organization for Applied
Research (The Netherlands; dynamic furnace modeling), Technical University Graz & Bios Bioenergy Systeme (Austria; CFD-based furnace design), Vyncke (Belgium; furnace construction) the National Swedish Testing Institute (Sweden; advisory role), the Instituto Superior Técnico (Portugal; dissemination), Eindhoven University of Technology (development of CFD modules for the fuel layer and gas phase). This international project group proved to be an interesting working environment in which different viewpoints on grate furnace combustion could meet.

The results described in this thesis have been published and presented at national and international congresses. Initial studies into a simple model with analytical solutions to describe the conversion of a solid fuel layer was presented at various annual national symposia (Burgers Dag, NPS-symposium, Combura, FOM-Dagen, Physics@Veldhoven in the period 2003-2008) and at an international conference in Salzburg, 2005. This work has now been accepted for publication [1] and can be found in Chapter 4 of this thesis. The extension of the numerical model with a more detailed representation of the chemistry was presented at the International Biomass Conference in Berlin, Germany, 2007 and at the International Conference of Computational Science in Beijing, China, 2007. Subsequently, this analysis was published in Refs. [2,3]. The work in chapter 6 is partly based on these publications. Finally, an experimental and numerical study of the role of heat losses in reverse combustion experiments was performed that is described in chapter 5. We have the intention to publish this study in the near future.

There are also results of the project that are not presented in this thesis. During my Ph.D.-project, we presented the results of an experimental and theoretical study of biomass conversion in a grid reactor at the International Biomass Conference in Rome, Italy, 2004. This study that was performed during my graduation project at Faculty of Applied Physics under the supervision of professor Rini van Dongen. At the 4th European Combustion Meeting in Louvain La Neuve, Belgium, 2005, we presented results aimed at the validation of gas phase combustion models to describe NO\textsubscript{x} formation in a grate furnace. Both the work with the grid reactor and the gas phase combustion models was continued by co-workers in the Combustion Technology group.

During the project, I was supported by a large number of people. Here, I would like to thank some of them. First, I would like to thank my promotor, professor Philip de Goey who gave me the opportunity to work on biomass conversion and to develop my professional skills. I would like to thank my first co-promotor Rob Bastiaans for his critical, but constructive comments that contributed to the quality of my work. I would like to thank my second co-promotor Jeroen van Oijen for shared with me his knowledge about the laminar flame code CHEM1D in which I implemented the solid fuel conversion model. Professor Bert Brouwers, professor Theo van de Meer and professor Gerrit Brem have carefully read the manuscript of this thesis, which resulted in significant improvements in the text.

The Combustion Technology group and the division Thermofluids Engineering offered a pleasant working atmosphere. I would like to thank all my colleagues (Ph.D. students, postdocs, scientific staff and supporting staff) for this.

The representatives of the OPTICOMB project partners offered a challenging and stimulating environment due to the opportunity to learn more about the viewpoints
of other research institutes and engineering firms. I would like to thank Robbert van Kessel, Arij van Berkel, Richard Arendsen, Maarten Jansen (TNO), Robert Scharler, Emil Widmann, Selma Zahirovic (TU Graz), Claes Tullin (SP), Hans Fastenaekels (Vynke) and Zdena Zsigraiová (IST) for this.

Various Bachelor and Master Students contributed to the results that can be found in this thesis. Michiel Geurds, Martijn van Graafeiland, Mbelwa Katunzi, Lalit Agarwalla, Martijn Goorts, Gerben Jans and Pascal Bovij are acknowledged for this.

My work for the board of the Young Energy Specialists and Development Cooperation, a Dutch, national organization of young professionals active in the energy section, enabled me to place my work in a broader social and economic perspective. I would like to thank all my fellow board members (Haike van de Vegte, Gerard Stienstra, Jolien Snellen, Joost van Stralen, Diana Ros Riu, Maarten Mangnus) for this.

Finally, I would like thank some people for more personal support. The group of friends that I made during my studies, which is informally known as ‘Het Opportunistisch Borrelgenootschap’ (Mark Bax, Martijn Toll, Menno van den Donker and Gerrit Kroesen) has preserved the pleasant and inspiring atmosphere that I experienced during my studies. Gemmeke Groot, Happy Bongers, Armand Smits and Michiel Peters are also acknowledged for their personal. Finally, I would like to thank my family. My parents Jan and Ludy and my brother Frank have always supported me in pursuing my goals.

Eindhoven, April 2008,

Hans van Kuijk
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Chapter 1

Introduction

1.1 Introduction

Clean and efficient combustion of renewable fuels is essential to stop climate change and to decrease our dependency on fossil fuels. Grate furnace combustion is a much-used conversion technique for solid fuel conversion. In this thesis, a numerical and experimental study of the conversion of a solid fuel layer in a biomass fired grate furnace is described.

The results presented in this thesis contribute to the optimization of biomass combustion in grate furnaces by achieving a combustion process with minimal nitrogen oxides emissions. The method followed is the development of a numerical model for the conversion of the solid fuel layer. This model is developed to serve as part of a Computational Fluid Dynamics (CFD) model that can be used to study the optimal furnace design and operating conditions.

This chapter starts with a discussion of the social and economic background of the work described in this thesis (Sec. 1.2). It is followed by a short introduction into grate furnace conversion technology (Sec. 1.3) in which the principle of grate furnace combustion, models of grate furnaces and the conversion of the solid fuel layer are described. Finally, the aim and outline of this thesis are presented (Sec. 1.4).

1.2 Background

The greenhouse effect and the security of the energy supply are the two main reasons to increase the use of renewable energies in our energy mix. The greenhouse effect is mainly caused by the emission of CO$_2$. These emissions result for more than 80% from fossil fuels used for the production of energy (cf. [4]). The severe consequences of these emissions for our climate are becoming increasingly visible (cf. [5]).

The concern about the security of our energy supply is caused by the concentration of the production of oil in a small number of countries with large reserves (OPEC members in the Middle East, Venezuela, and Russia). This situation has resulted in supply disruptions by geopolitical events and increasing oil prices. Be-
cause of these events, a secure energy supply is currently placed at the top of the international political agenda (cf. [6]). In particular, a renewable and secure supply of energy is a major objective of the energy policy of the European Union [4]. With this policy, the European Union aims at a reduction of greenhouse gases of 20% in 2020 and 50% in 2050 compared to 1990 levels and a decrease of the large share of imported fossil fuels in the total energy mix (cf. [6]).

The use of biomass can play an important role in achieving the goals of the policy of the European Union. The conversion of biomass is CO\(_2\) neutral, i.e. it does not contribute to the greenhouse effect. In addition, its production is not limited to a small region, but it can be grown at almost every location in the world. It can be grown in the EU member states itself or it can be imported from other countries.

The most important advantage of the use of biomass over other sources of renewable energy is the possibility to apply it on the short term. Existing furnaces and conversion techniques originally developed for fossil fuels can operate on biomass fuels with no or only small modifications. Gate furnace combustion, which is studied in this thesis, is an example of this, as grate furnaces originally have been used for the conversion of coal (cf. [7]) and waste (cf. [8]). Another example is the co-combustion of biomass in existing pulverized coal fired power plants, which is widely applied in the Netherlands. The use of biomass derived synthetic fuels (e.g. pure vegetable oil, biodiesel, ethanol) in internal combustion engines, which has already led to a share of 3.75% in the total fuel consumption in Germany [9], is also a good example.

Biomass has also other important advantages. Unlike wind or solar energy, the supply of biomass is less dependent on external influences. In case of wind energy, the varying wind force strongly affects the energy yield of wind farms, while in case of solar energy cloudiness can temporary reduce the energy yield. In addition, biomass can be easily stored, which is not the case for wind and solar energy. Furthermore, it can lead to economic growth in developing countries when they become involved in the production of biomass (cf. [10]). The European agricultural sector can also benefit significantly from growing biofuels [4].

It is still a challenge to produce biomass in a sustainable way. Sustainability is a term that pertains to a number of social and environmental aspects related to biomass production and transport (cf. [11]). One of these aspects consists of the considerable CO\(_2\)-emissions related to the production and transport of biomass. Another aspect is a possible increase of food prices due to competition for land and water between biomass crops and crops grown for the food supply. Increasing food prices could make it more difficult for developing countries to secure their food supply. Finally, the production of biomass can lead to a decrease of the biodiversity or may harm the environment otherwise. The replacement of rain forest by biomass plantations in Indonesia and Brasil is an example of this.

Recently, the sustainability issue received increased attention (cf. [12]) and the idea for an international certification system for biomass has been put forward (cf. [11]). A certification system can ensure that the biomass produced in the European Union or imported from abroad is produced in agreement with a number of clearly formulated sustainability criteria. Currently, an effort is made to convert a number of existing certification systems into an international certification system [11].
1.3 Grate furnace combustion

1.3.1 General conversion process

Grate furnace combustion is a widely used conversion method to obtain heat and power from biomass. It is typically used for applications with a nominal thermal capacity of roughly $0.1 - 100$ MW [13,14]. In the Scandinavian countries and Austria, several hundreds of these plants exist [13, 15]. Most of these plants are used to combust residues of wood industry. Grate furnaces can deal with a wide range of biomass fuel types (e.g. sawdust, wood pellets, bark, fibreboard) and are flexible regarding fuel size and moisture content [14]. Grate furnace combustion is also applied to convert solid municipal waste (cf. [8,16,17]) and coal (cf. [18]).

The combustion process in a grate furnace (cf. Fig. 1.1) is divided into two steps. In the first step, the solid fuel is gasified on a moving grate by an airflow supplied at the bottom of the fuel layer. The air flows though the void space in between the fuel particles constituting the fuel layer. The layer is ignited by the hot gases above it at the entrance of the furnace. The gasification step is a heterogeneous gasification process because the devolatalization and subsequent char oxidation involves both gas phase and solid phase species. (In addition, homogenous gas phase reactions in the void space of the fuel layer take place but these are not primary responsible for the conversion). During the gasification process, the fuel is transported over the grate through the furnace, until all fuel is converted at the end of the grate. Due to the conversion process, the height of the fuel layer decreases towards the end of the grate. The heterogeneous gasification process occurs only on the grate. In the second step, burnout of the gases takes place [14]. This is a purely homogeneous process that takes place in the other parts of the furnace. When the combustion process is finished, the gases release their heat to a heat exchanger.

Different types of grate furnaces exist, because the furnace can be optimized for various fuels and operating conditions. In particular, different types of grates can be found. A traveling grate consists of an endless band transporting the fuel through the furnace with minimal disturbance of the fuel layer. A moving grate pushes the fuel over the grate by bars moving relative to each other, which also causes local mixing of the fuel layer. Other types of grates are fixed grates, inclined grates and vibrating grates. [14]. For moist fuels, preheated primary air can be used to enhance ignition. In addition, flue gas recirculation can be used to improve the mixing of the combustible gases and to control the temperature in the furnace [19].

Grate furnace combustion gives rise to emissions. One of these emissions consists of considerable amounts of $\text{NO}_x$. The $\text{NO}_x$ emissions are caused by oxidation of nitrogen present in the solid fuel, because due to the relatively low temperatures in the furnace (typically $1100 - 1400$ K) the oxidation of $\text{N}_2$ is negligible [13]. Typical $\text{NO}_x$ concentrations resulting from grate furnace combustion are 100-200 ppm for fuels with a low nitrogen content, whereas for fuels with a high nitrogen content, the emissions may increase to 300-800 ppm [14].

Because the emission of $\text{NO}_x$ into the atmosphere leads to acid precipitation, vegetation damage, smog formation, corrosion and material damage [14] emission standards have been developed which have to be met by combustion furnaces, among
which are grate furnaces. In the Netherlands, the emission standard for biomass
fired furnaces is BEES (Besluit emissie-eisen stookinstallatie milieubeheer) [20]. In
this standard, currently a limit of $100 \text{ mg m}^{-3}$ for installations $< 300 \text{ MW}$ is given,
corresponding to $50 \text{ ppm}^2$. The emission limits in BEES are strict in comparison
with the typical emissions of grate furnaces and have become more tight during the last
decades (cf. table 1.1). Although the Dutch regulations are strict in comparison with
other other European countries the trend in restricting these emissions further can
also be observed in the rest of Europe (cf. [14]).

A technique implemented in grate furnaces to limit the emissions of $\text{NO}_x$ is
staged combustion. This involves the division of the combustion chamber in a sec-
ondary and a primary combustion zone with each their own supply of air. The
difference between these combustion zones is the ration of the air supply to the fuel
supply. The primary combustion zone is kept at fuel rich conditions. This has the
result that in the primary combustion zone, a considerable part of the fuel-N, i.e.
fuel nitrogen, is released as $\text{N}_2$. Due to the low temperatures in the furnace, further
conversion into $\text{NO}_x$ is prevented. Therefore, this limits the formation of $\text{NO}_x$.

In the secondary zone, burnout of the gases coming from the primary zone takes
place. The combustion process in the secondary zone is oxygen rich to ensure com-
plete burnout of the gases. However, only a small excess of secondary air is required
because the mixing process of reactants is much better for a homogenous process
than for a heterogenous process. The small air excess is also a factor that helps to
reduce the $\text{NO}_x$ emissions. The fuel-N that is not released as $N_2$ by the solid fuel is re-
leased in the form of so-called N-precursors $\text{NH}_3$ and HCN. These N-precursors flow

---

1Here, $\text{mg m}^{-3}$ stands for the mass of the pollutant present in 1 m$^3$ of flue gas at a temperature of
288K and a pressure $p = 101.3 \text{ kPa}$ without moisture [20].

2Assuming that all nitric monoxide is converted into $\text{NO}_2$, 1 mg m$^{-3}$ $\text{NO}_x$ is equivalent to 0.49
ppm
1.3 Grate furnace combustion

<table>
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<th>Time</th>
<th>Emission limit NO(_x) (mg \cdot m(^{-3}))</th>
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<tr>
<td>Before August 1, 1988</td>
<td>650</td>
</tr>
<tr>
<td>August 1, 1988 - October 14, 1992</td>
<td>500</td>
</tr>
<tr>
<td>October 15, 1992 - December 31, 1993</td>
<td>200</td>
</tr>
<tr>
<td>January 1, 1994 - Present</td>
<td>100</td>
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Table 1.1: Emission limit for installations <300 MWth according to BEES-A [20]

together with the other gases to the primary combustion zone. The low primary air excess has the effect that it reduces the part of the N-precursors is converted into NO while it promotes the formation of N\(_2\). Thus, also in the secondary combustion zone, the formation of NO\(_x\) is limited. Consequently, the staged combustion process results in low NO\(_x\) emissions and good burnout of the gases.

It can be concluded that grate furnace combustion is a mature combustion technique for which already a range of techniques are available to optimize it for specific types of fuels, good burnout of the exhaust gases and low NO\(_x\)-emissions. However, the decreasing emission limits show that there is a continuous effort of governments to lower the emissions further. Furthermore, the increased demand for biomass fuels described in the previous section may lead to an increase of fuel costs, thus pushing operators of grate furnaces to use low cost fuels like waste wood. However, these fuels have a high nitrogen content due to the contamination by paint and other additives. Thus, research is needed to develop, optimize and implement emission reduction techniques. The model for the solid fuel layer can be used for this purpose.

1.3.2 Grate furnace modeling

The model presented can help to reduce NO\(_x\) emissions from grate furnace combustion by means of using Computational Fluid Dynamics (CFD) models. These models have proven to be a cost-effective method for optimizing grate furnace combustion [19] and can be used to predict the exhaust gas composition [21, 22]. CFD models usually consist of two parts: 1) a fuel layer model, describing the heterogeneous conversion process on the grate, and 2) a turbulent gas phase combustion model for the gas phase combustion in the primary zone (above the fuel layer) and the secondary zone. The coupling between the two models is done by means of matching the boundary conditions for the mass, species and energy fluxes.

The gas phase combustion models consist of a models that describes the fluid dynamics of gas flow in combination with a model for the combustion process. For the turbulent flow, the k,epsilon model is used generally to describe the fluid dynamics. For the combustion model, significant development has taken place. Initially, a simple model based on determination of the rate limiting step of turbulent mixing or the kinetics of a small number of global reactions has been applied, the EDM (Eddy Dissipation Model) (cf. [21]). An important improvement has been made by applying the EDC (Eddy Dissipation Concept) [23] to a grate furnace. This models enable the use of detailed kinetic mechanisms (cf. e.g. [24]) to describe the combustion process, which is necessary to describe the evolution of the N-precursors
to of NOx [25]. Recently, an flamelet based combustion model was used for a grate furnace [22]. This model makes use of lookup tables for the chemistry based on laminar flame calculations (‘flamelets’), which leads to a considerable reduction of calculation time and an improved description of the interaction between chemistry and turbulence. Further development this approach will make it computationally affordable to perform parametric studies to improve the furnace design.

The improvements of the gas phase models means that also improved fuel layer models are required. Due to the complexity of the conversion of solid fuel, this is a challenging task. Initially, a model based on empirical data was used to obtain the properties of the gases above the solid fuel layer [21]. Models that represent the conversion process in the solid fuel layer have mainly been used for stand-alone studies, i.e. they have not been coupled to a gas phase combustion model. In recent years, these fuel layer models have been improved considerably. First, simple models with a single step heterogenous reaction have been used to describe the conversion process [16]. This was followed by models in which the conversion process is described in more detail and which also include expressions for gas phase oxidation in the interparticle space in the bed (e.g. [26, 27]). Currently, models have been developed that describe the conversion of the solid fuel layer on the basis of calculations on the level of single particles level (e.g. [28–30]). However, detailed models of the release of the nitrogen precursors from the solid fuel layer have not been developed yet.

1.3.3 Conversion of the solid fuel layer

In this section, the general principle of the gasification process of the fuel on the grate are described to illustrate the requirements for a fuel layer model. First, it is shown that the conversion process is effectively one-dimensional, which greatly facilitates the development of models. Then, the main parameters governing the conversion process are identified and described. Finally, an overview is given about the interaction of the main parameters related to the conversion process.

For a traveling grate, i.e. a configuration in which no mixing of the fuel layer takes place, the conversion process consists of a reaction front propagating through a porous fuel layer in the opposite direction of the air flow. This process is known in the literature as reverse combustion [1, 30] and is in good approximation one-dimensional, ignoring gradients along the grate (cf. e.g. [27, 30]). The spatial coordinate indicating the horizontal position on the grate can be transformed to a time coordinate in a 1D description (Fig. 1.2). To do so, the horizontal distance $\Delta x$ that a section of the fuel layer has traveled over the grate has to be be divided by the grate velocity $v_G$, i.e.

$$t = \frac{\Delta x}{v_G} \tag{1.1}$$

can divided by the timeThis means that the conversion process can be studied experimentally in a fixed bed reactor (cf. e.g. [17,31,32]) and theoretically with 1D models (cf. e.g. [16,27,30]). From a modeling point of view, the combustion process for other types of grates is highly similar, because the mixing effects can be accounted for by introducing an empirical mixing coefficient in the 1D model.
1.3 Grate furnace combustion

A fixed bed reactor (cf. Fig. 1.3) consists of a cylindrical tube with an inner radius \( R_i \) and an outer tube radius \( R_o \). Generally, the reactor is insulated, resulting in an outer radius \( R_o \). An air flow is applied at the unburnt side \( u \). Usually, the mean superficial gas velocity at the unburnt side, \( V_{gu} \), is used to indicate the magnitude of the air flow. The interstitial air velocity, i.e. the true gas velocity in the void space of the fuel layer, is indicated with \( v_g \). These velocities are related by \( V_g = \epsilon v_g \), where \( \epsilon \) indicates the porosity of the fuel layer. In the conversion front, the solid fuel is converted into gaseous and solid products. The solid products consist of ashes and, for small values \( V_{gu} \), also of char.

The parameters related to the conversion process in a fixed bed reactor can be divided into four groups:

- **Fuel properties.** These properties include the moisture content, the elemental composition, the chemical structure, particle size, porosity of the fuel layer, etc.

- **Operating conditions.** This group includes the applied gas velocity, the oxygen mass fraction in the primary air, primary air temperature and primary air moisture content.

- **Reactor design parameters.** These parameters contain the reactor diameter, the wall thickness and wall material as well as the material and thickness of the insulating layer around the setup.

- **Process parameters.** These include the velocity and temperature of the reaction front and the composition of the exhaust gases.

The parameters of primary importance are the velocity of the conversion front, \( v_{su} \), and the gas velocity \( V_{gu} \). The velocity of the conversion front is dependent on the fuel properties, operating conditions and reactor design parameters. Furthermore, it determines the stoichiometry of the conversion process and is thus directly related to the composition of the product gas and the temperature of the reaction front. The gas velocity has the largest effect on \( v_{su} \) and is thus the main operating parameter to control the combustion process in a grate furnace.
The solid conversion front velocity is typically $v_s \sim O(10^{-2})$ cm s$^{-1}$, which means that the typical time for a reverse combustion experiment is $O(1)$ h. Measured temperatures during the conversion process are in the range of $1100 - 1400$ K. Of course, these values are merely indicative and are dependent of fuel, operating conditions and reactor design.

In this thesis, results are presented in terms of mass flows instead of velocities because these quantities give a more precise insight in the stoichiometry of the conversion process. The gas mass flow at unburnt conditions is defined by $m_{gu} = \rho_{gu} \epsilon_u V_{gu}$, while the solid mass flow at unburnt conditions is given by $m_{su} = \rho_s (1 - \epsilon_u) v_{su}$. The solid mass flow is also referred to as ignition rate in the literature (cf. e.g. [16,33]), as it represents the amount of fuel that is ignited per unit surface area per unit time. On the basis of the definitions of $m_{gu}$ and $m_{su}$, the stoichiometric ratio $r_S$ can be defined as

$$r_S = \frac{m_{su}}{m_{gu}}. \hspace{1cm} (1.2)$$

In contrast to for example a laminar premixed flame, the stoichiometry of a reverse combustion process is not determined by the concentration of fuel and oxidizer in the unburnt region. In a reverse combustion process, a certain gas mass flow is applied. The fuel properties, operating conditions and reactor design parameters then result in a certain velocity of the reaction front from which a value for $m_{su}$ can be determined. This means that for reverse combustion, $r_S$ can only be determined a posteriori on the basis of results of models or experiments.

A sketch of the main combustion process parameters as a function of $m_{gu}$ (Fig. 1.4) shows that $T_f$ and $m_{su}$ have a maximum as a function of $m_{gu}$. At a certain value $m_{gu,e}$ extinction of the flame takes place [16]. Spatial profiles of $Y_{O_2}$ and the temperature $T$ show that $Y_{O_2}$ decreases in the region of the reaction front, while the temperature $T$ increases. The profile of $T$ is dependent of the presence of heat losses. These heat losses can occur in fixed bed experiments heat transport out of the reaction zone through the reactor walls to the environment. In the presence of heat losses, $T_f$, the maximum temperature, is located in the region of the conversion front. Due to the heat losses, $T$ decreases to $T_u$ for $z \to \infty$. For adiabatic conditions, $T_f$ remains constant, i.e. $T_b = T_f$.

The general description of reverse combustion given in this section is concluded by describing the terminology introduced in Ref. [16] for the characterization the combustion process on the basis of the exist gas composition. A distinction of three combustion regimes is made, dependent on the air flow. The partial gasification regime occurs at low air flows. In this regime, the available oxygen is insufficient to reach complete conversion of all ignited solid fuel. The carbon in the solid fuel is converted mainly into CO; only low concentrations of $CO_2$ are formed. In addition, the low oxygen supply results in the presence of a growing layer of char on top of the reaction layer. The char layer is the reason for the designation ‘partial gasification regime’: only part of the solid fuel is gasified, while the other part remains in the solid state in the form of char. In the complete gasification regime, all ignited fuel is converted into gases because the applied air flow is larger. However, the carbon in the solid fuel is still mainly converted into CO. In the combustion regime, complete oxidation takes place. The line indicated with $S$ in Fig. 1.4 represents com-
1.4 Aim and outline

The aim of this study is the development of a reverse combustion model using detailed chemistry that can serve as part of a larger model for a complete grate furnace. The description of the chemistry in the model should be of sufficient quality to be able to predict the release of the N-precursors from the solid fuel layer. In addition, the main parameters related to the conversion process have to be predicted by the model, because these create the conditions for the N-release. Other requirements to the model is that it should have reasonable calculation times and that it should give predictions that can be validated with experiments.

In Chap. 2, the possibilities and quality of existing models is investigated by means of a literature review. In addition, in this chapter a summary is given about the data available to develop models for the conversion of a solid fuel layer with more detailed chemistry.

In Chap. 3, a general formulation of the equations used for the reverse combus-

![Figure 1.3: Sketch of a fixed bed reactor](image)
Figure 1.4: Sketch of combustion process parameters. Left: $m_{su}$ and $T_f$ as a function of $m_{gu}$. The line representing stoichiometric conditions is indicated with $S$. Right: spatial profiles of $T$ and $Y_{O2}$. Spatial temperature profiles for non-adiabatic ($T_f$, solid line) and adiabatic ($T_b$, dashed line) conditions.

Chapter 3 consists of an investigation whether an existing analytical solution to the model equations (cf. [16]) can be used to describe the conversion process on the grate. Analytical solutions have the advantage that offer an explicit solutions for the main parameters of the combustion process, which makes it unnecessary to perform numerical calculations. The use of an analytical solution for the combustion process would therefore be very efficient from a computational point of view. However, to arrive at analytical solutions, approximations in the model equations and the solution procedure have to be made. The investigation performed in this chapter focusses on comparison between analytical and numerical solutions to find out the consequences of these approximations. Such a comparison has not been made by the developers of this model (cf. [16, 34]) and therefore it is made here.

A second goal of the study described in Chap. 3 is to find out whether a stationary formulation of the 1-D version of the model equations presented in the previous section is an efficient method to obtain numerical solutions. Such a method can be applied because the conversion front behaves like a stationary traveling wave during the larger part of the conversion process. The use of such a stationary formulation for 1-D fixed bed models has not been applied in other studies in the literature.

Chapter 4 is concerned with the experimental validation of one dimensional models. Heat transport effects in experimental reactors may lead to values for $v_s$ and $T_b$ that deviate significantly from their adiabatic values resulting from 1D models. These effects consist of heat losses to the environment, instationary heating of the reactor walls and preheating of the unburnt fuel by means of conduction by the reactor walls to the unburnt region. It is investigated by means of experimental and numerical methods to which extend these heat transport effects affect the combustion process and how parameters related to the design of the reactors influence this.
1.4 Aim and outline

Current 1-D reverse combustion models have limited capacity of dealing with the chemistry of the combustion process, while this is important to predict the evolution of N-species. In Chapter 5, it is investigated if measurements of the release rates of chemical species from single particle experiments can be used in a reverse combustion model. In addition, it is investigated whether detailed kinetic mechanisms based on elaborate set of chemical species and reactions, can be used to describe the chemistry in the void space of the fuel layer.

Finally, in Chap. 6 general conclusions of the experimental and numerical study in this thesis are presented and recommendations for future work are given.
Chapter 2

Literature overview reverse combustion

2.1 Introduction

In this chapter, an overview existing knowledge of fixed bed conversion is presented and areas that require further research are identified. First, the methods used for previous studies are described. This chapter starts with a description of existing models and their properties (Sec. 2.2). Three classes of models are identified while one of these classes, the numerical 1-D model, is described in detail. This is followed by an overview of setups and measurement techniques used for experimental studies (Sec. 2.3) followed by a description of different types of models and their properties (Sec. 2.2). Then, experimental and numerical results of previous studies are used to describe the effect of fuel properties, operating conditions, reactor design parameters and model parameters on the combustion process (Sec. 2.4). Subsequently, kinetic data for homogenous and heterogenous reactions that has not yet been applied to fixed bed combustion is presented. This is followed by a discussion of the results of the literature overview (Sec. 2.6). Finally, conclusions are presented (Sec. 2.7).

2.2 Models

2.2.1 Model classes

Reverse combustion is a complex phenomenon. This has resulted in the development of different types of models that differ in solution method (analytical or numerical), purpose (e.g. offering insight in the combustion process, getting predictions of the gas phase composition above the fuel layer, investigate the effect of single particle behavior) and application area (submodel) for biomass grate furnace combustion, coke fuel layers, small cellulosic fibres). The existing models can roughly be divided into three classes:

- Simple 1-D models
  These models make use of a limited set of equations that is simplified up to a
point where analytical solutions can be found (cf. [16, 34–36]) and are usually used to describe reverse smolder. Reverse smolder is a subclass of reverse combustion and is characterized by conversion by direct attack of the oxygen on the solid fuel particles, i.e. there are no flames formed due to homogeneous gas phase reactions [37]. It mainly occurs at low air flows and for very small fibres, for example cellulose or polymer fibres (cf. e.g. [38]).

- **Detailed 1-D models**
  The second class of models ((cf. e.g. [30, 39]) consists of 1-D models that are solved numerically. These models contain a more detailed description of the conversion process of the fuel layer. In these models, the heterogenous conversion of the fuel layer is described with devolatalization kinetics, while generally also several reactions are included for the gas phase combustion process. Some of these models contain a source term based on separate single particle models (cf. e.g. [28, 29, 40]). These models are all developed to describe the conversion of wood. In the past, also 1D models have been developed for fixed bed coal gasification processes (cf. e.g. [41]), but the current state of the art models for wood combustion are more advanced, because they include more phenomena.

- **Detailed multi-dimensional models**
  A third class of models use detailed 2D and 3D numerical simulations to completely resolve the fuel layer with a size of the grid cells much smaller than the particle diameter (cf. [42, 43]).

Analytical solutions are particularly advantageous when the solution is to be incorporated into reactor models predicting dynamic reactor behavior as a result of changing operating or feedstock conditions (cf. [16]). The reason for this is the explicit expressions for process parameters they offer which makes it unnecessary to use numerical methods that are computationally more costly.

A familiar example of a successful application of an analytical model for solid fuel conversion is the lumped reaction source term model for single coal or char particles that is used in many numerical and analytical descriptions involving the overall conversion of groups of these particles in e.g. a fuel layer (cf. [16, 44]). Such a source term results from a solution for a particle that reacts with partially mass transfer limited surface reaction. This solution is exact for a first order reaction (cf. [45]) and is a good approximation for higher order reactions.

Other examples of application of analytical solutions can also be found. In Ref. (cf. [46]), an analytical solution to a pyrolysis model for wood particles is applied in a circulating fluidized bed model. Furthermore, in Refs. (cf. [47, 48]) a model for the nonlinear conversion of a porous solid particle in a gas is presented that is used for several applications: char combustion in fluidized beds, the combustion of pulverized coal and the gasification of cokes. In particular, the model has been applied in a coal fired fluidized bed combustor to predict overall efficiency and emissions.

Another advantage of using analytical solutions is the insight they offer in the combustion process. With analytical solutions, the principles of reverse combustion have been described and understood. The effect of $m_{gu}$ on $T_f$ and $m_{su}$ (cf. Fig. 1.4)
was successfully explained (cf. [35]). The initial increase of $m_{gu}$ enhances the reaction rate which leads to an increase of $T_f$ and $m_{su}$. However, with further increasing $m_{su}$ the transport of heat out of the reaction zone increases also. The latter effect becomes dominant at high air flow rates and leads to a decrease of $m_{su}$ that finally results in extinction when $m_{su} = 0$.

The models with analytical solutions have been used to study several phenomena related to reverse combustion:

- **Heat losses**
  In Ref. (cf. [35]), a small heat loss term was included in the 1D transport equations. It was shown that the effect of small heat losses results in (1) a decrease of the calculated values for $m_{su}$, (2) a threshold value of $m_{gu} > 0$ below which no propagating front occurs and (3) a decrease of the value of $m_{gu,E}$ for which extinction takes place.

- **Reaction source term dependent on the solid mass fraction**
  A reaction source term not only dependent on the oxygen mass fraction but also on the conversion of the solid fuel was introduced by Schult [36]. His results show that extinction can occur while $m_{su} > 0$ because complete conversion of the solid prohibits the generation of additional heat necessary to sustain the flame if $m_{gu}$ is increased further.

- **Reaction source term lumped by mass transfer**
  In Refs. [16, 34], a model is presented that includes a source term that can describe the effect of transport limitations of mass and heat from the convective flow to the particles through a boundary surrounding the particle. This model was applied to conversion of coke and wood.

The 1-D numerical models combine a detailed description of the conversion process with moderate calculation times. Examples of a detailed description are the use of multiple step heterogeneous reactions for devolatilization and char oxidation as well as the description of several gas phase species by multiple transport equations.

Detailed multidimensional models for combustion of solid fuel (cf. [42,43]) can describe the conversion of solid fuel by resolving not only the gradients of the reaction front, but also the intraparticle gradients. Initial 3D results have been obtained by using a single step chemical reaction. The model results show the importance of resolving the interparticle and intraparticle gradients, and therefore justify the approach of direct numerical simulations. The model is expected to be able to predict the production of pollutant species like CO and NO$_x$ [43]. A disadvantage of using such a model is that it is computationally intensive.

From these three types of models, the detailed 1D models offer the best opportunity for use in a CFD model aimed at improving the design of a grate furnace. Both simple 1D models and detailed 1D models are suitable to use for process control in a grate furnace, although the possibilities of analytical models are somewhat limited due to the lack of detail.
2.2.2 Properties of detailed 1D numerical models

The 1D numerical models offer the best opportunity for application in a grate furnace. We discuss the features of these models in more detail here. The physics, chemistry and model configuration are described subsequently in this section.

Physics

The physics of the model consists of the governing equations to describe the transport of mass and heat, together with the expressions for coefficients in these models. In addition, drying, particle shrinkage and radiation are physical phenomena.

- **Transport equations**
  The models generally consist of conservation equations for the gas and solid phase. The conservation equations are written for mass, energy (in terms of temperature or enthalpy) and species mass fractions. In order to describe the transport of heat and mass in the fuel bed, heat and mass transfer coefficients as well as dispersion coefficients are used in these equations. The heat and mass transfer coefficients describe the transport of heat, reactants and products through the boundary layers surrounding reacting single particles in the fuel bed. The dispersion coefficients describe the spreading of heat and mass due to the variation of microscopic streamlines with respect to the mean direction of the flow [49]. In general, fixed bed models make use of the expressions summarized by Wakao (cf. [50]) for all these coefficients.

- **Drying**
  Multiple approaches exist to describe drying. In the model of Thunman [30] vaporization is described by a single step reaction with an Arrhenius expression for the rate constant to release moisture at the boiling point. Wurzenberger [28] uses an equilibrium model wherein the liquid water in the particles is in equilibrium with the local gas phase. Yang [26] uses two expressions for the drying rate. The first expression describes the drying process for $T < 373 \text{ K}$ as a process dependent of the local heat transfer and the concentration difference of moisture in the gas phase and solid phase. The second expression describes the drying process at $T > 373 \text{ K}$ as a function of the evaporation heat and the heat absorbed by the solid. Shin [51] uses a single expression for the drying rate based on an expression that includes a mass transfer coefficient and the concentration difference of moisture between the gas and the solid phase.

- **Shrinkage**
  Shrinkage is the effect of decreasing particle volume during conversion. By using an equation for the change in porosity of the fuel bed, this can partly be taken into account. However, because in all models the porosity is directly related to the density of the fuel bed, this is insufficient. For example, a drying process will lead to a change in density of the fuel bed, but the wood particles will not change much in size because the water is mainly present in the void space of the wood. Therefore, the porosity of the fuel bed will not change
much. Thunman [30] takes into account shrinkage of the particles by means of applying shrinkage factors for the subsequent conversion of moist wood into dry wood, char and ash. In the bed model (cf. [30]) the volume change is taken into account by coordinate transformation based on a scaling of the ratio of the instantaneous particle volume over the original particle volume. A similar approach was proposed by Ohlemiller (cf. [37]). Other models (cf. e.g. [26, 27, 51]) do not deal with particle shrinkage.

- **Radiation**
  The effect of energy transport in the solid fuel layer by radiation is included in most models. In a minority of the models, the Rosseland approximation is used: the effect of radiation is taken into account in the expression of the thermal dispersion coefficient (cf. e.g. [28, 52]). The majority of the models uses a more detailed radiation model, e.g. the Schuster-Swarzschild two flux model (cf. e.g. [26, 30, 51, 52]). In this model, an additional equation for the radiation fluxes in the fuel layer is solved.

**Chemistry**

The chemistry in the model consists of the species represented, devolatalization, char oxidation, gas phase reactions and N-chemistry.

- **Species**
  The species resolved in the solid phase are fuel, moisture, char and ash for most models. The species that are taken into account in the gas phase are generally $\text{N}_2$, $\text{O}_2$, $\text{CO}_2$, $\text{H}_2\text{O}$, $\text{H}_2$. Some models take into account the presence of tars. The composition of these tars is generally determined from the mass balance of the pyrolysis process. In some of the models, multiple tar species are used (cf. [30, 52]) (i.e. $\text{C}_i\text{H}_j$ to represent the lower hydrocarbons, $\text{C}_i\text{H}_j\text{O}_k$ for the higher hydrocarbons), in others the volatiles are considered to be a single product (cf. [28]). The composition of the volatiles, $(i, j$ and $k)$ is calculated from a mass balance.

- **Devolatalization**
  For the heterogenous devolatalization process, simple models using a single reaction or multiple step reactions are used. Thunman [30] and Johansson [52] use a single step approach based on the three-step mechanism of Chan, [30, 52]. Johansson use a single step with a rate that is the sum of the rates of the parallel three step mechanism of Chan. Johansson [40] also uses the expression of Miller and Bellan, which has separate rate expressions for the wood components cellulose, hemicellulose and lignin. Yang [26] used a single step model to test several rate expressions described in the literature. Wurzenberger [28] used the parallel reactions model developed by Alves and Figuerdo and Antal with separate rate expressions for the individual gaseous species, one tar species and char. Van der Lans [27] used a single step reaction on the basis of TGA experiments based on three different heating rates.
• Char oxidation
Several approaches are used to describe char oxidation. Thunman [30] and Johansson [52] use a four step mechanism that includes oxidation, gasification by CO$_2$, H$_2$O and H$_2$. Wurzenberger [28] uses a three step mechanism with similar reactions as Thunman but no char gasification by H$_2$. Yang [26] uses only a single oxidation reaction. In all models, rate limitations of the kinetic rate by mass transfer are accounted for by lumping the reaction source term with a mass transfer coefficient. To predict the ratio CO/CO$_2$ most models use correlations based on experimental data (cf. e.g. [26,30,52]). Van der Lans [27] points out that theoretical expressions for this ratio are not in agreement with his measurements and therefore puts it on a fixed value. Shin [51] does not take into account this ratio because he uses a single char gasification reaction with CO as the only product.

• Gas phase reactions
For the homogenous combustion of the gas phase species, generally a small set of reactions is used. Thunman [30] and Johansson [52] use reactions for oxidation of CO and H$_2$, include the water gas shift reaction (forward and reverse) and combustion reactions for tar compounds representing the light and heavy tars. The reaction rate of the light tars is based on methane combustion, whereas for the heavy tars, a rate expression based on the cyclic structures of these compounds is used. In the work of Yang [26], for simplicity all volatiles are considered to be a single product $C_mH_nO_l$. This product is then converted into CO and H$_2$ by a single step reaction. The oxidation of CO and H$_2$ is described by two oxidation reactions. A water-gas shift reaction is not included. Wurzenberger [28] uses an overall reaction for secondary tar conversion of tars into CO, CO$_2$, CH$_4$, H$_2$ and a inert tar component. Furthermore, this study includes four homogenous gas phase reactions are included: three for the oxidation of CH$_4$, H$_2$, CO and the water-gas shift reaction. Shin [51] uses an oxidation reaction for CO and a conversion reaction for a single volatile species consisting of $C_xH_y$ into CO and H$_2$O.

• Nitrogen chemistry
The N-chemistry and N-release has been taken into account in the model of Yang (cf. [53]). In this model, it is assumed that the N-release during the propagation of the reaction front is in the form of NH$_3$ only. The De Soete model (cf. [54]) is described to model the conversion into NH$_3$ or NO or N$_2$ in the gas phase. Thus, the description of the N-chemistry currently available in fixed bed models is limited and coarse.

Model configuration
The model configuration consists of the dimension of the model, the boundary conditions and the inclusion of a single particle models. As all model discussed in this section are 1-D, only the boundary conditions and the use of a single particle model are described here.
2.2 Models

- **Boundary conditions**
The boundary conditions determine how the fuel is ignited (boundary conditions at the reactor outlet) and represent the operating conditions (boundary conditions at the reactor inlet). At the reactor outlet, usually a heat source is included used to ignite the fuel layer (cf. e.g. [30, 52]) which is switched off after a certain of time.

- **Reactor walls**
Thunman introduces an instationary term in the 1D model to describe the effect of the heating of the reactor walls on the combustion process (cf. [30]).

- **Particle model**
A particle model is used in some studies (cf. e.g. [28, 30, 52]) to describe the fact that the gas and solid phase are not in thermal equilibrium due to intraparticle transport of heat. A particle model consists of a similar set of conservation equations as the bed model but are solved on a smaller scale with different coefficients. The particle model can be 1D (cf. [28, 30]) or 2D (cf. [52]). The exchange of heat and mass is given by the fluxes at the particle surface. These fluxes can be coupled to the bed model in which they form a source term. In some models, the coupling involves heat and mass transfer coefficients (cf. [28, 37]) that transport effects through the boundary layers of these particles, while in other models this effect is not accounted for (cf. e.g. [30]).

The detail in which the conversion process of the single particle is represented varies:

- Johansson [40, 52] does not couple the particle model completely to the bed, because the particle model is used to calculate an effective temperature for the solid phase. The effective temperature is then used in source terms in the bed model. In a completely coupled model, local temperatures in the particle are used to calculate these rates and the fluxes of mass and energy at the particle surface are used as a source term in the bed model (cf. e.g. [37]).

- Thunman [55] divides the particle in layers. Each layer represents one of the solid species: virgin wood, dry wood, char and ashes. This approach is able to describe the general features of the combustion process (cf. [30]), but is not able to make more detailed predictions, e.g. of the chemical species that are produced during the conversion process. Furthermore, the analysis presented by Thunman [56] illustrates that for particles with $d_p = O(1 \text{ cm})$ and $T > 600 \text{ K}$, drying fronts and pyrolysis fronts start to overlap. This effect becomes stronger for increasing $d_p$ and $T$.

- Wurzenberger [28] and Bruch [29] are able to solve the spatial profiles of gas phase species and temperature in the particle in detail.
2.3 Experimental setups

The reactors used in the experimental studies (cf. e.g. [16,33,57–59]) consist of cylindrical tubes with a typical diameter of $10 - 50$ cm and a height of $10 - 150$ cm. Generally, the reactors are insulated to prevent that heat losses to the environment affect the conversion process. To determine $T_f$, thermocouples are installed at different heights in the fuel bed. Also, $v_s$ can be derived from the thermocouple measurements. The latter quantity can be determined from the time it takes for the reaction front to travel between two thermocouples mounted at a fixed distance $\Delta z$ in the fuel layer. From $v_s$, $m_{su}$ can be determined. Usually, the setup is mounted on a weighing cell to determine the mass burning rate $m_b$, which is defined by

$$m_b = \frac{1}{A} \frac{dM}{dt}. \quad (2.1)$$

Here, $A$ is the cross-section of the reactor and $M$ the total mass measured by the mass balance. In the complete gasification regime and the combustion regime, $m_{su} \equiv m_b$, but in the partial gasification regime, $m_{su} > m_b$. The reason for this is the formation of char. The ignition rate takes into account the amount of ignited fuel per unit surface area per unit time. It does not matter whether the fuel is converted into char or gas. In the determination of $m_b$, only the fuel that is converted into gases is accounted for. In case of char formation, this is smaller than the amount of fuel ignited.

Determination of the mass fractions of gas species in the flue gas has been performed with a wide range of techniques. The concentration of main gas components (i.e. CO, CO$_2$, CH$_4$ and O$_2$) as well as NH$_3$ have been measured with dispersive infrared techniques (NDIR) [16, 32]. Measurements with a paramagnetic sensor have been applied to determine the O$_2$ concentration [16, 51]. Fourier Transform Infrared Spectroscopy (FTIR) has been applied to measure the concentration of the main gas components, as well as NH$_3$, HCN, NO$_2$ and N$_2$O [31, 32]. Measurements with a Flame Ionization Detector (FID) have been used to determine the total fraction of hydrocarbon species C$_x$H$_y$ [16, 27, 32]. Gas Chromatography (GC) has been used to determine the concentration of H$_2$, N$_2$, CH$_2$ and O$_2$. [32]. Wet analysis has been applied to measure HCN and NH$_3$ [31, 32]. The concentration of NO and NO$_2$ was also determined with chemiluminescence technique [31].

2.4 Parameter studies

The parameter studies that have been performed in fixed bed combustion concern the effect of operating conditions and fuel properties on the process parameters are described in this section. The group of reactor design parameters, potentially important, is not represented here due to the lack of systematic studies into these effects. Furthermore, a new group of parameters in this section is introduced: the model parameters. This group consists of parameters that are difficult to vary in experiments but can be changed easily in a model, e.g. the activation energy of the devolatalization reaction(s).
2.4 Parameter studies

2.4.1 Operating conditions

The following operating parameters related to the air flow have been investigated:

- **Air flow** \((m_{gu})\)

  The gas mass flow influences the main process parameters strongly. The effect of \(m_{gu}\) on \(m_{su}\), \(T_f\), and \(Y_{O_2,u}\) discussed in Sec. 1.3.3 was already described in 1934 in a discussion of experiments performed by Nicholls [33]. This study was performed using coal as a fuel. Later experimental studies confirmed that this result is generally valid for solid fuel conversion in the reverse combustion mode. (cf. e.g. [16,51,57]).

  Several modeling studies (cf. [16,40,52,60]) have shown that the effect of \(m_{gu}\) on \(m_{su}\) can be described with . The results of Gort [16] for \(m_{su}\) as a function of \(m_{gu}\) are acceptable considering the small number of equations he used. The predicted values for \(m_{su}\) are within 25% of the measurements for both coal and wood beds. However, in case of coal beds, heat losses had to be accounted for in the energy equations for the coal bed, while in case of the wood bed, the pre-exponential factor in the Arrhenius-rate had to be fitted.

  The comparison between model results and experimental data made by Yang [26] indicates that the trend in the measured values of \(m_{gu}\) is predicted correctly. The order of magnitude of the predicted \(m_{su}\) is correct, but deviations of 30% in \(m_{su}\) occur. The deviations for high values of \(m_{gu}\) could be caused by channeling. This is the effect that due to local non-uniformities in the flow, air can pass the front without reacting [53].

  Johansson [52] shows that the predictions of his model for \(m_{su}\) as a function of \(m_{gu}\) follow the correct trend and are within the experimental error of around 15% when compared the data of Refs. [16,61]. In most other publications, validation of the model for a range of \(m_{su}\) is not presented. Generally, results for a very limited number of values of \(m_{gu}\) are presented (cf. e.g. [27,28,30]).

- **Air temperature** \((T_{gu})\)

  The effect of air preheating was investigated in several experimental studies (cf. e.g. [16,17,33]). For coal and coke beds, an increase of \(m_{su}\) of roughly factor 1.5 has been observed when the temperature of the air flow, \(T_{u}\), was increased from 300 K to 700 K [33]. For dry wood particles, \(m_{su}\) more than doubles when the primary air with a temperature of 273 K is used, while for wood particles with a moisture content of 10% the increase is only 20% [16].

  It was observed by Van Kessel [17] that air preheating in combination with a moist fuel can lead to a division of the conversion process in two phases. In the initial phase, a reaction front propagates in the moist fuel bed, while due to the hot air flow a drying front starts to move upward. The final phase starts at the ‘breakthrough’ time, when the reaction front and the drying front meet. The reaction front then starts to propagate through a hot, dry fuel bed, which leads to a very rapid conversion process in comparison with the initial phase.

- **Air oxygen content** \((Y_{O_2,u})\)

  Variation of the oxygen content in the applied air flow is discussed in Ref.
When the amount of oxygen in the air flow increases, $m_{su}$ increases strongly, while $T_f$ decreases. Increasing the concentration of oxygen in the gas flow from 16% to 25% resulted in an increase of $m_{su}$ from $0.3 \text{ g cm}^{-2}\text{s}^{-1}$ to $3.5 \text{ g cm}^{-2}\text{s}^{-1}$ and an decrease of $T_f$ from 1600 K to 1000 K.

### 2.4.2 Fuel properties

In the studies reported in the literature, a wide range of fuels has been used. The fuels range from coke and coal (cf. e.g. [16,33]) to particles of various kinds of wood (cf. e.g. [57,59]), sawdust [62], pelletized wood (cf. e.g. [32,62]), bark (cf. e.g. [32,61], straw (cf. [27]), fibre board (cf. [31]) and solid municipal waste (cf. [16]). However, there are only limited reports about systematic comparisons between fuels in which fuel properties have been studied one by one. Here, it is attempted to distinguish the effects of four fuel properties: volatile content, particle size, moisture content and nitrogen content.

- **Volatile content**

  The fuel volatile content was studied by Nicholls [33] and Gort [16]. Nicholls observed that a fuel with a higher volatile content generally leads to an increase of the observed values of $m_{su}$ and results in an increased value of $m_{gu,e}$.

  Gort studied the effect of fuel volatile content by means of wood particles that were partly devolatalized before the start of a fixed bed experiment (cf. [16]. The effect of the devolatalization time on $m_{su}$ and $T_b$ showed no clear trend, possibly due to the presence of moisture during the pyrolysis process (cf. [16]).

- **Particle size**

  The effect of particle size, represented by an (effective) particle diameter $d_p$ has been studied by Nicholls, Gort and Rönnback. The effect of $d_p$ is strongly dependent on the volatility of the fuel. For coke, a non-volatile fuel, a strong decrease of $m_{su}$ was observed with increasing particle size (cf. [16,33]), while such a strong increase is not observed for wood (cf. [16]).

  The difference between wood and coal regarding particle size was explained in Ref. [16] by the rate limiting conversion mechanism, which in case of non-volatile fuels consists of a gas-solid reaction on the particle surface, while in case of volatile fuels a volumetric pyrolysis process takes place. As a change in particle size leads only to a change in effective surface area and not in the bed porosity, the effect of particle size is stronger for low volatile fuels.

  There is still debate in the literature on the effect of particle size for wood particles, partly because the effect is only small [61]. The measurements of Gort [16] show an increase of $m_{su}$ of the order of 10% for an increase in particle size from 1 to 3 cm. The measurements of Rönnback show a slight increase in of $m_{su}$ with increasing $d_p$ in the range 0.8 – 3 cm. Results of Ryu [59] show a decrease of $m_{su}$ of 5% when the particle size was increased from 0.5 cm to 20 cm.

  Results of modeling work for wood conversion do not give a decisive answer. Results of Yang [63] show an maximum value of $m_{su}$ at $d_p = 1$ cm. Model
results of Thunman [64] show a decrease in $m_{su}$ of almost 25% when $d_p$ is increased from 0.3 cm to 3 cm.

- **Moisture content**
  An increase of the moisture content of the fuel yields a strong decrease in $m_{su}$ and $T_f$. In Ref. [16], it was shown that an increase in the moisture content from 10% to 30% was shown to lead to a decrease of 30% in $m_{su}$ and a decrease in the maximum value of $T_f$ of 100 K. Similar results were found by others (cf. e.g. [51, 60]).

A parametric model study with respect to moisture content has been performed by Yang (cf. [26, 60]). This study shows that an increase of the mass fraction of water in the fuel leads to a strong decrease of $m_{su}$. An increase of $Y_{s,H_2O}$ of 0.1 to 0.5 leads to a reduction of $m_{su}$ with a factor 8, while the extinction point shifts from $m_{gu,E} = 6.0 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$ to $m_{gu,E} = 1.8 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$. This was in agreement with experimental results.

- **Nitrogen content**
  The fate of the fuel nitrogen in fixed bed was determined in several experimental studies (cf. [27, 31, 32, 62]). Samuelsson [32] measured the gas phase composition during front propagation in a batch of pelletized sawdust. These measurements show that at the oxygen-rich, unburnt side of the reaction zone, the major nitrogen compound in the gas phase is $\text{NO}$. This means that the N-precursors released in this part of the reaction zone are rapidly oxidized. At the burnt side, where the oxygen is almost depleted, the major nitrogen compound is $\text{NH}_3$. This means that the NO produced in the oxygen rich part of the reaction zone is converted into $\text{NH}_3$ again downstream of the reaction zone, where the oxygen is depleted. Finally, the main N-compound present downstream of the reaction zone in the burnt gas mixture is shown to be $\text{N}_2$ ($O(60\%)$), while the main N-precursor is $\text{NH}_3$ ($O(30\%)$). For an increasing air ratio, results show that the share of $\text{N}_2$ increases at the expense of the share of $\text{NH}_3$.

The results of Samuelsson are confirmed by the studies of Weissinger [31] using fibreboard (a fuel with high N-content of 3.4) due to chemical additives) and Van der Lans [27]. Experiments performed by Widmann [62] show that for sawdust significant contributions of $\text{NH}_3$ were detected in the flue gas stream of around 100 ppm, whereas the amount of $\text{NH}_3$ detected was in the order of 200 ppm. This could be caused by the small particle size, resulting in decreased hydrogenation of HCN released in the center of the particle [25].

During char burnout, $\text{NO}$ is the major product [32]. During the front propagation phase, the partitioning of the fuel-N show a slight enrichment of the N-content of the char (i.e. the mass fraction of nitrogen in the char becomes higher than in the original wood). This contributes to the formation of $\text{NO}$.

### 2.4.3 Model parameters

The effect of the following model parameters has been investigated:
• Devolatization kinetics
Yang [26] tested several expressions for the kinetics of a single step devolatilization reaction ranging from slow to fast. From this study, it can be concluded that the choice for the devolatilization kinetics has an insignificant effect on the results for \( m_{su} \) because drying is the rate limiting step during conversion. However, effects are noticeable with respect to other parameters. For instance, the char production increases significantly when the rate of the reaction increases. The results of Yang are confirmed by Johansson [52], who finds a difference of only 10% in \( m_{su} \) when the rate expressions for the kinetics of Miller and Bellan [65] are compared with the kinetics of Chan [66] et al.

• Radiation model
The effect of the radiation model was studied by Johansson (cf. [52]), who compared a two-flux radiation model with a radiative conductivity model. The use of the two flux model results in a value of \( m_{su} \) that is 10% higher than the value obtained with the radiative conductivity model. Such differences fall within the experimental error.

• Particle model
Several authors include a detailed particle model in their 1-D model (cf. e.g. [28–30, 52]). A comparison of the impact of the particle model was presented by Thunman [64], who observed that a separate particle model is only required for large particles \((O(30 \text{ mm}))\). Due to the absence of large gradients in the temperature, a particle model is not required for small particles \((O(30 \text{ mm}))\). Johansson [40] tested a 2D particle model. Such a model can take into account situations in which the width of the combustion front is of the same order of magnitude or smaller than the width of the reaction zone. Results show that the difference in \( m_{su} \) of the 1D particle model with the porous medium approach was 19%, while this difference was only 13% in case of the 2D particle model (results for \( d_p = 4 \text{ cm} \)). This means that the porous medium approach underestimates the effect of the particle size on the front velocity, while with the use of a 1D particle model it is overestimated.

2.5 Chemistry
Kinetic data used in a reverse conversion model is required to obtain accurate results for the prediction of \( Y_{ig,b} \), the gas phase composition above the fuel layer. The heterogenous kinetics determine the release of N-precursors and the distribution of fuel-N over char, tar and gases. The evolution of the N-precursors in the gas phase needs to be described with appropriate mechanisms for the heterogeneous kinetics. Here, overviews of the kinetic data available for a description of the heterogeneous (Sec. 2.5.1) and homogenous (Sec. 2.5.2) reactions are presented.
2.5 Chemistry

2.5.1 Heterogenous reactions

The heterogenous processes occurring in the reaction zone consist of devolatalization and char oxidation. The devolatalization of the wood particles in the fuel layer is in good approximation a pyrolysis process (cf. Fig. 2.1a). Due to a rapid outflow of the product gasses during the larger part of the devolatalization phase, oxygen cannot reach the particle surface. Instead, the oxygen is consumed by the homogenous reactions in a diffusion flame surrounding the particle. This is not the case for char combustion, where the oxygen is involved in a heterogenous surface reaction (cf. Fig. 2.1b).

This section aims at a description of the devolatalization phase of the conversion process, because due to the release of N-precursors it is essential for \(\text{NO}_x\) predictions. A description of how to include char oxidation has already been presented (cf. Sec. 2.2.2). A more detailed description of char oxidation can be found in literature about coal conversion (cf. e.g. [67, 68]). A description of \(\text{NO}\)-formation from char-N can be found in Ref. [25].

Kinetic data for devolatalization is usually obtained from TGA (ThermoGravimetric Analyzer) studies. With a TGA apparatus, a small \(O(\text{mg})\) sample of biomass is heated isothermally in an oven by applying a user defined temperature profile \(T(t)\). The heating process takes place in a chemically inert environment by flusing the oven with nitrogen or argon. During the heating process, the mass of the sample is recorded. From the measurement data, i.e. mass loss versus temperature, kinetic parameters for the devolatalization process can be obtained. Several kinetic

Figure 2.1: Sketch of the conversion process of fuel particles: devolatalization phase (a) and char combustion phase (b). The mass fractions \(Y_v\) and \(Y_p\) refer to the total mass fractions of volatiles and products of gas phase combustion, respectively.
schemes have been used in this process consisting of a limited number of reactions (single step, parallel, consecutive or both)(cf. [69]). These models offer insight in the chemistry of pyrolysis and are useful to determine the global quantities of char, tar and gas.

Recently, the species that are released during devolatalization have been determined by a combination of TGA and FTIR (Fourier Transform Infrared Spectroscopy) techniques in an TGA-FTIR setup. The setup was developed and used by Wojtowicz and coworkers (cf. e.g. [70–72]) and has resulted in detailed data of 17 gaseous species, ranging from simple species (e.g. CH$_4$ and CO) to more complex species (e.g. phenol (C$_6$H$_5$OH) and acetone (CH$_3$OCH$_3$)). The measured species account for 40 – 60% of the total volatile release. The data also includes release rates for HCN and NH$_3$.

The results of the TGA-FTIR experiments have been modeled with the FG-DVC-model [72,73]. This model is based on the distributed activation energy approach [72]. The distributed activation energy approach makes use of the assumption that the total release rate of single gas phase species from the solid fuel is given by a range of reactions with different activation energies. This range is specified by a distribution function with empirical parameters that can be obtained from the TGA-FTIR experiment. The heating rates used in the experiments to determine the empirical parameters are in the range 10 – 100 K s$^{-1}$. This is lower that the heating rates typically observed in reverse fixed bed combustion experiments (cf. Chap. 6) but it is assumed that the FG-DVC model can be used to extrapolate the experimental data to higher heating rates (cf. [72]).

Heated grid techniques have been used to determine conversion rates under high heating rates conditions. In this technique (cf. [67,74]) a small amount (O(1 mg)) of pulverized fuel (fibre size O(10 µm)) is converted on a small electrically heated grid (O(1 cm)). With this setup, data at high heating rates (O(10$^3$) K s$^{-1}$) can be obtained. Until recently, this has been applied for measurements of CO and CO$_2$ only. By using FTIR analysis instead of laser absorption diagnostics, diNola [75] measured the end yield of several gaseous species for conversion processes with heating rates in the range of 600 – 1000 K s$^{-1}$. Results include data for NH$_3$ and NO.

In the review paper of Glarborg (cf. [25]) the present understanding of the release of N-precursors from solid fuel is summarized. It is pointed out that during the devolatalization process the fuel-N is distributed over the gases, tars and char. Measurements show that for temperatures in the range 600 – 1200 K the nitrogen is preferentially retained in the char. During secondary pyrolysis of char and tar, mainly NH$_3$ is released. The light nitrogen species formed during primary and secondary pyrolysis mainly consist of HCN and NH$_3$. It is well established that the nitrogen volatiles partitioning depends on fuel type, devolatalization temperature and heating rate. A fuel type with a higher volatile content, the lower the HCN/NH$_3$-ratio. Higher heating rates appear to decrease the HCN/NH$_3$-ratio for biomass. In addition, large particles seem to favor the production of NH$_3$ over the production of HCN. The reason for this is most likely a reaction of HCN to NH$_3$ during the residence time in the particle. Higher heating rates and smaller particle sizes cause a decrease in residence time and thus a decrease of the HCN/NH$_3$-ratio.
2.6 Discussion

2.5.2 Homogeneous reactions

For gas phase combustion, detailed kinetic mechanisms are available. The mechanism developed by Smooke [76] describes the essential reactions for methane combustion and contains 13 species and 25 reactions. One of the first reaction mechanisms available for the modeling of NO\(_x\) formation in gaseous flames was the development of the Miller-Bowman mechanism [77]. The GRI-Mechanism has been developed more recently and is optimized for the combustion of natural gas [78].

A mechanism that can be used to model NO-formation in biomass combustion is the SKG (Skreiberg-Kilpinen-Glarborg) mechanism [24]. This mechanism is recommended for modeling the reduction of NO\(_x\) by primary measures in the combustion of biomass, because it was validated under the conditions resembling the conversion of early nitrogenous volatile species in a staged combustion process. It is reliable for modeling the oxidation of ammonia at moderate temperatures (i.e. < 1400 K) and at fuel rich conditions [24]. This makes the mechanism suitable to use for reverse combustion modeling.

During the conversion of biomass, a considerable amount of nitrogen is converted to the volatile species. The composition of the volatile species is still a subject of investigation, but application of new methods to describe the formation of tars during coal pyrolysis has already lead to an identification of tars up to molecular masses of 312 atomic mass units. [79]. Furthermore, the kinetics of higher hydrocarbons is also subject of investigation. For example, a reaction mechanism for the combustion of benzene has already been developed(cf. [80]). Benzene is one of the major tar compounds released during biomass gasification (cf. [81]).

2.6 Discussion

In this chapter, models for reverse combustion as well as available kinetic data are described. The overview of models shows that the 1-D model, solved either numerically or analytically, is the best approach for a description of the fuel layer in an overall CFD model for a grate furnace. For the 1-D models with analytical solutions, the main reason for this is the low computational effort because explicit expressions for model solutions can be used. For the 1D models with numerical solutions, the main reason is the combination of reasonable calculation times with detailed predictions of the gas phase composition. Furthermore, the description of the parameter studies performed with these models shows that they are capable to predict the effect of a range fuel properties, operating conditions and model parameters on the combustion process.

From the overview given this chapter, it becomes also clear that three issues related to reverse combustion modeling require additional attention:

1. Can heat and mass transfer effects be represented by means of analytical models?

Analytical models have not been used to study the effect of single particle mass and heat transport on the combustion process, while these effects can become important for larger particles used in practical grate furnace conver-
sion processes. The only analytical model that takes into account these transport effects is presented in Refs. (cf. [16, 34]). For the analytical solution to be valid, the lumped reaction source term in the model should have an exponential dependence on the temperature (cf. [34]). However, this is not the case when transport effects start to dominate the conversion process. Therefore, the validity range of the analytical solution should be investigated with respect to the role of transport effects.

2. Is the increase of model complexity of 1-D models justified?
This question can be raised for three reasons. Firstly, a comparison between the description of the 1D models and the parameter studies shows that the number of parameters in the models is larger than the studies performed to investigate the effect of these parameters on the conversion process. Secondly, there are model features that have not been validated experimentally. An example for this is the inclusion of the single particle model in 1-D models. Measurements of the front velocity, temperature and gas phase composition have not shown that including a particle model leads to better predictions. An important reason for this are inaccuracies in the experimental determination of $m_{ss}$. Thirdly, the 1-D models should be computationally efficient to be usable in an overall CFD model for the complete furnace. Unjustified complexity leads to unnecessarily long calculation times.

3. Can available kinetic data be used in reverse combustion models to predict NOx-formation?
Currently, there is data available about the heterogenous and homogeneous chemical process occurring in the reaction zone, but this data is not used in fixed bed models. At the same time, this is required to predict the formation of NOx. The kinetic data is not complete in the sense that all the species released from the solid fuel layer can be modeled, but the data that is available can already be used. Furthermore, the investigation of the release rates of volatile species including N-precursors and the modeling of a more extensive set of gas phase species is a topic of ongoing research which will lead to results that can directly be applied in fixed bed models.

In Chap. 4, issues 1 and 2 are addressed. The first issue, the investigation of the validity range of the analytical model presented in Refs. (cf. [16, 34]) by means of a comparison to numerical solutions is the main topic described in Chap. 4. The second issue, the justification of the increased model complexity, is addressed by testing whether a simple model having analytical solutions can be used to describe a reverse combustion process. In addition, in this chapter it is investigated how the implementation of the numerical solution method of this simple model can be such that the computational costs remain low.

In Chap. 5, issue 2 is addressed. Increasingly detailed fixed bed models have to be validated with accurate measurements. One of the parameters that can affect the measured value of the front velocity in a fixed bed experiment are heat losses to the reactor walls and to the environment. These heat losses will be affected by the reactor design parameters (i.e. the conductivity of the reactor walls). The reactor design
parameters have not been investigated by modeling studies and experiments. Only the work of Thunman [30] includes a term in the model equations to account for the instationary heating of the reactor walls, but the magnitude of this effect is not accounted for. Therefore, Chap. 5 contains a numerical and experimental investigation of these effects.

Chapter 6 is concerned with issue 3. In order to predict the evolution of the fuel nitrogen into gaseous nitrogen compounds, heterogeneous (TGA-FTIR measurements) and homogenous (gas phase reaction mechanisms) kinetic data is implemented in the fixed bed model and results for the evolution of N-compounds are obtained.

2.7 Conclusions

The literature overview presented in this chapter has resulted in the identification of three issues for further research needed to arrive at accurate and efficient models for conversion of the solid fuel layer in a grate furnace. These issues consist of (1) a further investigation of the incorporation of single particle heat and mass transport effects in analytical models, (2) investigation whether the complexity in existing reverse combustion models is justified and (3) a need for implementation of available kinetic data in fixed bed models to predict NO\textsubscript{x}-formation. These issues will be addressed in the following chapters of this thesis.
Chapter 3

Model equations

3.1 Introduction

In this chapter, a reverse combustion model is used to perform the research described in chapters 1 and 2. The equations of the model are written down in a general form. This ensures that for each of the chapters that follow, an appropriate version of the general set can be used in a 1D or 2D formulation.

The outline of this chapter is as follows. First, the governing equations are presented (Sec. 3.2). Then, the expression for the homogeneous reaction source term is given (Sec. 3.3). Subsequently, the solvers used for the model are described (Sec. 3.4). Finally, conclusions are presented (Sec. 3.5).

3.2 Governing equations

The governing equations of the model are presented in this section. These equations can formally be derived by averaging transport equations on the microscopic scale. Such a procedure is outlined in Ref. (cf. [49]). Here, only the macroscopic equations are presented. The conservation equation for the solid mass is given by

\[
\frac{\partial}{\partial t} \left((1 - \epsilon) \rho_g \right) = \sum_{i_s} \dot{\omega}_{i_s}^{gs}.
\]  

(3.1)

The left hand side of this equation contains the unsteady term, while the term on the right hand side represents the net source of mass due to heterogenous reactions. Here, \(\epsilon\) is the porosity, \(\rho_s\) is the density of the solid and \(\dot{\omega}_{i_s}^{gs}\) the mass source term of solid phase species \(i_s\) due to heterogeneous reactions. In this work, heterogenous reactions are defined as reactions that involve at least one species of each phase. The source term \(\dot{\omega}_{i_s}^{gs}\) is defined as an effective source term accounting for both reactions at the particle surface and in the interior of the particle. The homogenous reactions do not contribute to the source of mass of the solid phase and are therefore not represented in this equation. The conservation equation for solid phase species \(Y_{i_s}\) is given by

\[
\frac{\partial}{\partial t} \left((1 - \epsilon) \rho_s Y_{i_s} \right) = \dot{\omega}_{i_s}^{gs} + (1 - \epsilon) \dot{\omega}_{i_s}^s.
\]  

(3.2)
Here, the right hand side contains source terms of species \( i \) resulting from heterogeneous (\( \dot{\omega}_{gs}^{h} \)) and homogenous (\( \dot{\omega}_{gs}^{h} \)) reactions. In this work, a formulation of conservation of energy in terms of the enthalpy is used. For the solid phase enthalpy \( h_s \) this equation is

\[
\frac{\partial}{\partial t} \left( (1 - \epsilon) \rho_s h_s \right) - \nabla \cdot \left( (1 - \epsilon) \frac{\Lambda_s}{c_{ps}} \nabla h_s \right) = \dot{\omega}_{gs}^{h}.
\]  

(3.3)

Here, \( \Lambda_s \) is the heat dispersion tensor, \( c_{ps} \) the specific heat of the solid material and \( \dot{\omega}_{gs}^{h} \) the enthalpy source term due to heterogenous reactions. The enthalpy of phase \( \psi \) is defined as

\[
h_{\psi} = \sum_{\psi} Y_{i\psi} h_{i\psi}, \quad \psi = g, s
\]

(3.4)

where \( h_{i\psi} \) is the enthalpy of mixture component \( i \) in phase \( \psi \). It is given by

\[
h_{i\psi} = \int_{T_{\text{ref}}}^{T} c_{pi} \psi dT_{\psi} + h_{i\psi}^{0},
\]

(3.5)

where \( h_{i\psi}^{0} \) is the enthalpy at standard temperature and pressure. The standard temperature is indicated by \( T_{\text{ref}} \).

For the gas phase, a similar set of equations can be written. The mass conservation equation for the gas phase is given by

\[
\frac{\partial}{\partial t} (\epsilon \rho_g) + \nabla \cdot (\epsilon \rho_g v_g) = \sum_{ig} \dot{\omega}_{gs}^{g}.
\]

(3.6)

In this equation, the second term on the left hand side represents convective transport. In this equation, \( \rho_g \) is the gas phase density, \( v_g \) the interstitial gas velocity (i.e. the gas velocity in the void space of the fuel layer) and \( \dot{\omega}_{gs}^{\text{het}} \) the reaction source term of gaseous species \( i_g \). The conservation equations for the gas mass fractions \( Y_{i_g} \) are given by

\[
\frac{\partial}{\partial t} (\epsilon \rho_g Y_{i_g}) + \nabla \cdot (\epsilon \rho_g v_g Y_{i_g}) - \nabla \cdot (\epsilon \rho_g D \nabla Y_{i_g}) = \dot{\omega}_{gs}^{g} + \epsilon \dot{\omega}_{sg}^{g}.
\]

(3.7)

The third term in this equation represents dispersive transport, while the last two terms are source terms due to heterogenous and a homogenous reactions respectively. In the dispersive term, \( D \) represents the mass dispersion tensor. The enthalpy equation for the gas phase is given by

\[
\frac{\partial}{\partial t} (\epsilon \rho_g h_g) + \nabla \cdot (\epsilon \rho_g v_g h_g) - \nabla \cdot \left( \frac{\epsilon \Lambda_g}{c_{pg}} \nabla h_g \right) = \dot{\omega}_{gs}^{g}.
\]

(3.8)

The enthalpy equations (cf. Eqs. 3.3, 3.8) contain a source term \( \dot{\omega}_{gs}^{g} \) which has not been specified. In this work, it is modeled by

\[
\dot{\omega}_{gs}^{g} = - \sum_{i_g} h_{i_g} \dot{\omega}_{i_g}^{g} + \alpha_T S (T_s - T_g).
\]

(3.9)
3.3 Gas phase chemistry

Here, the first term on the right hand side represents the source of enthalpy related to the exchange of species between the two phases, while the second term represents the exchange of heat. The symbol $\alpha_T$ is a heat transfer coefficient and $S$ is the internal surface area of the fuel bed per unit volume. By using Eq. 3.9 it is assumed that the release of heat by heterogenous reactions takes place in the solid phase. In Appendix A a further explanation of this term is presented.

The density of the gas phase is calculated from

$$\rho_g = \frac{p_0 M}{R_g T_g},$$  \hspace{1cm} (3.10)

where $p_0$ is the ambient pressure and $R_g$ the universal gas constant. A momentum equation for the pressure $p$ is not solved, as this quantity is nearly constant in the fuel bed, i.e. $p = p_0$. The average molar mass $\overline{M}$ is defined as

$$\overline{M} = \left( \sum_{i_g} \frac{Y_{i_g} M_i}{M_g} \right)^{-1}. \hspace{1cm} (3.11)$$

The density of the solid is taken constant in this thesis:

$$\rho_s = \rho_{s0}. \hspace{1cm} (3.12)$$

### 3.3 Gas phase chemistry

This section deals with the specification of the reaction source term due to homogeneous gas phase reactions. It follows the discussion presented Ref. [82]. The oxidation of gaseous fuel mixtures is governed by many elementary reaction steps. Before presenting the general expression for the reaction source term, the contribution of only one elementary reaction is considered. As an example, we consider the reaction

$$\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O} \hspace{1cm} (3.13)$$

in which oxygen ($\text{O}_2$) and atomic hydrogen ($\text{H}$) react to form the radicals hydroxyl and oxygen ($\text{O}$). The reaction rate $r_f$ is assumed to be proportional to the concentrations of the reactants:

$$r_f = k_f [\text{O}_2][\text{H}], \hspace{1cm} (3.14)$$

where the square brackets denote the concentration $\rho_g Y_{i_g}/M_{i_g}$ of species $i_g$ and $k_f$ denotes the reaction rate coefficient. The subscript $f$ indicates that the forward reaction is considered. The reaction rate coefficient is usually written in a modified Arrhenius form,

$$k_f = A_T^\beta \exp(\frac{E_a}{RT}), \hspace{1cm} (3.15)$$

with $A$ and $\beta$ reaction constants and $E_a$ the activation energy (J mol$^{-1}$). For a homogenous system, the concentration of the species involved will change in time due to the reaction as follows:

$$\frac{d[\text{OH}]}{dt} = \frac{d[\text{O}]}{dt} = -\frac{d[\text{O}_2]}{dt} = -\frac{d[\text{H}]}{dt} = -r_f. \hspace{1cm} (3.16)$$
In general, the species reaction may occur also in opposite direction:

$$O_2 + H \leftarrow OH + O$$  \hspace{1cm} (3.17)

The reaction rate of this reversed reaction is denoted by $r_r$ and the net reaction rate of the forward and reverse reactions (3.13) and (3.17) is given by

$$r = r_f - r_r = k_f [O_2][H] - k_r [OH][O_2].$$  \hspace{1cm} (3.18)

The reaction coefficient of the reverse reaction $k_r$ can be obtained by using the equilibrium constant

$$k_{eq}(p, T) = \frac{k_f}{k_r}$$  \hspace{1cm} (3.19)

In general, a homogenous gas phase reaction numbered $j_g$ can be written as

$$\sum_{i_g} \nu'_{i_g,j_g} M_{i_g} \rightleftharpoons \sum_{i_g} \nu''_{i_g,j_g} M_{i_g},$$  \hspace{1cm} (3.20)

where $M_{i_g}$ represents species $i_g$ and $\nu_{i_g,j_g} = \nu''_{i_g,j_g} - \nu'_{i_g,j_g}$ represent the stoichiometric coefficients, which indicate how many molecules take part in reaction $j_g$. In a practical combustion process, the reaction order, $\sum_{i_g} \nu'_{i_g,j_g}$, of the reactions involved will not exceed three. Reaction (3.13) is an example of a second order reaction, which is the most common.

The general expression for the reaction rate of reaction (3.20) reads

$$r_{j_g} = k_{f_{i_g,j_g}} \prod_{i_g} \left[ M_{i_g}^{\nu'_{i_g,j_g}} \right] - k_{r_{i_g,j_g}} \prod_{i_g} \left[ M_{i_g}^{\nu''_{i_g,j_g}} \right]$$  \hspace{1cm} (3.21)

The total source term as it appears in the conservation equations for the species contains the contribution for all chemical reactions:

$$\dot{\omega}_{i_g} = M_{i_g} \sum_{j_g} \nu_{i_g,j_g} r_{j_g}$$  \hspace{1cm} (3.22)

### 3.4 Solving the equations

In this thesis, the model is used in a 1D and 2D version. For the 1D approach, the model is implemented in the 1D reactive flow code Chem1d. This code is used because it can deal with detailed chemistry, which is necessary for NO\textsubscript{x} predictions. Furthermore, the adaptive gridding technique available reduces the computational effort without compromising the accuracy of the results. Chem1d was originally developed by Somers et al. (cf. [83]) and has been successfully applied in much recent studies (cf. e.g. [84–86]). A more detailed description of the code and the gas phase data it uses can be found in (cf. [82,83]).

A 2D approach is required to model heat losses in a fixed bed reactor. For the 2D approach, the commercially available package ‘Comsol’ is used, because it enables convenient methods to perform calculations in 2D and 3D geometries of different...
size and shape. However, this package cannot deal with detailed chemistry and is therefore used with a simplified set of reactions.

The data required to solve the equations is not discussed further in this chapter. We only mention here that for the data for $c_{p_i}$ and $h_{i,g}$, polynomial correlations are used for which the coefficients are supplied together with the reaction mechanisms used. Data for the other quantities is described in the subsequent chapters at the moment it becomes relevant.

### 3.5 Conclusions

A general formulation of the model equations describing reverse combustion is presented. The model is able to describe transport of heat and mass as well as heterogeneous and homogenous reactions in a two-phase system. The model is implemented in a 1D version to be used to model detailed chemistry in the fuel layer. A 2D version is available to model heat losses in a fixed bed reactor.
Model equations
Chapter 4

The effect of interparticle transport limitations on reverse combustion

4.1 Introduction

Fixed bed or fixed bed like conversion processes take place in many plants for conversion of solid fuel, for example coal gasifiers [41] and grate furnaces for biomass combustion [53,87]. To improve the efficiency and to reduce the emissions of these plants, CFD models are a helpful tool. In case of a grate furnace, an integral model consists of a submodel for the fixed bed combustion process in the solid fuel layer (primary combustion zone) and a submodel for the gas phase combustion (secondary zone). The model for the solid fuel layer should be able to describe the reverse combustion mode, in which most furnaces are operating. In this combustion mode, the conversion front is propagating in the opposed direction of the airflow (Fig. 4.1).

The submodel for the solid fuel bed should give accurate predictions for the temperature, composition and mass flow of the gas directly above the fuel bed. In the literature, either an empirical approach is used or numerical models are used. The empirical approach is directly based on fixed bed experiments and consists of correlations for the species and temperature of the gases directly above the fuel bed as

![Figure 4.1: Sketch of the reverse combustion process in a fixed bed.](image-url)
The effect of interparticle transport limitations on reverse combustion

A function of air flow rate [21]. Its disadvantage is the inflexibility to fuel properties, as a change in fuel type requires a new set of experiments. The numerical approach consists of a detailed description of the fixed bed combustion process. The numerical approach (e.g. [30, 53, 64]) has the disadvantage that due to its complexity it is difficult to explain deviations between model results and experiments. For example, the effect of particle size, which is closely related to the effect of heat transfer from and into the solid particles, is still not satisfactorily solved [64].

Analytical models can also be used to describe reverse fixed bed combustion. These models can describe the essential physical and chemical processes with only modest complexity. Generally, they contain just sufficient phenomena needed to describe the main parameters of combustion process, i.e. the flame velocity, temperature and converted fraction. On the other hand, the modest complexity makes them suitable to obtain insight in the effect of model parameters on the combustion process by giving explicit expressions for all variables. Existing analytical models [35, 36] have mainly been developed for a subclass of reverse fixed bed combustion: reverse smolder. In these problems the combustion process takes place by direct attack of the oxygen on the solid particle surface. With the models, the effect of air flow on the conversion front can be predicted and understood. The same holds for extinction mechanisms and heat losses. The results of these models have been compared to experiments for example polyurethane foams and cellulosic materials [38, 88]. The model predictions qualitatively agree with the smoldering of cellulosic materials [36] and give good quantitative predictions for the smoldering of polyurethane foams [89].

The disadvantage of the analytical models discussed here is their inability to take complex heat and mass transport effects into account. This means that they can only be applied to experiments with small fibre or particle size, such as the polyurethane foams and fine cellulosic materials. In case of beds of wood or coal, the particle size is generally much larger. Then, transport effects start to play a role. The nature of these transport effects is dependent on the fuel type. For wood particles, the conversion process consists of pyrolysis, during which combustible gases are produced, followed by the burning of these gases in a diffusion flame surrounding the particle. The pyrolysis rate is strongly controlled by the heat front moving from the surface of the particle towards the center of the particle [69]. For coal particles, the conversion rate is limited by transport of oxygen from the gas phase surrounding a particle to the particle surface [90].

Recently, an analytical model was presented in Ref. [34] that can take heat and mass transfer effects into account. In the model, transport effects are accounted for in the reaction source term. It is a method that is used commonly in the literature to describe heterogeneous reactions [45, 91]. The model can also be applied for flaming reverse combustion, as the slow heterogeneous processes are the rate limiting step. The effect of the rapid gas phase combustion process is a local heat release source at the location of the reaction front. This heat release source can be taken into account in the reaction enthalpy [16].

Although the model presented in Ref. [34] can describe the effect of transport limitations, the studies in which the model is discussed [16, 34] do not contain an analysis of the effect of the transport limitations on the structure of the flame. This
4.1 Introduction

effect is important for two reasons. Firstly, the flame structure is an important feature of the conversion process, as the combustion chemistry is determined by spatial profiles of reactant concentrations and temperatures. Secondly, the flame structure is closely connected to the method used to obtain an analytical solution. Without transport limitations, the high activation energy in the Arrhenius expression leads to a reaction wave structure with a distinct preheat zone and a reaction zone. Then, the use of the method of matched asymptotic expansions is justified. However, when transport effects are taken into account in the source term, the exponential dependence on the temperature is diminished and the flame structure alters. Although in Ref. [34] it is noted that for application of the model, the reaction rate near the maximum temperature should be exponentially large as compared to the reaction rate at lower temperatures, the consequence of transport effects in the source term for the accuracy of the model results are not discussed and quantified. Other studies referring to or discussing this model (cf. [92, 93]) have not yet addressed this issue.

The goal of this paper is to quantify the effect of transport limitations on the combustion process by means of a thorough numerical analysis of the model equations presented in Ref. [16, 34]. The first part of the analysis is performed to show the effect of transport limitations on the structure of spatial flame profiles. The flame profiles are obtained by solving the model numerically with a parameter set for the case of coal combustion. The second part consists of an investigation of the accuracy of the analytical solution for the coal parameter set. An error quantification is given by a means of a comparison of the analytical solutions with numerical results. Subsequently, the magnitude of the error is explained in terms of the flame structure.

The present work contains several important new results compared to the work presented in Ref. [16, 34]. Firstly, not only flame velocities but also dimensional spatial flame profiles for a realistic case are presented. The effect of transport limitations in the rate expression is illustrated with these profiles. Secondly, both stationary and instationary calculations are performed, whereas the analytical solution method results in stationary solutions only. The instationary results show that stable stationary solutions indeed exist, i.e. application of the stationary solution method is justified. Thirdly, the numerical solutions of the model equations presented here is proven to be an essential addition to the analytical solution method, because with the numerical calculations no a priori assumptions about the flame structure have to be made. This leads to results that are more general and more accurate than the analytical solutions. The error in the analytical results is determined by means of a comparison with numerical results. In kinetically controlled flames, the magnitude of the error is related to the inverse of the activation energy, which makes it possible to estimate it on the basis of analytical results only. For transport limited flames this is not the case, which means that numerical solutions are needed. In addition to these results, it should be noted that an important side-effect of the spatial flame profiles presented in this paper are the clues they give for the development of an improved analytical solution procedure.

While studying the results presented in this paper, it is important to keep in mind that the use of models that can be solved analytically brings about limitations in complexity. For reverse combustion, generally one or two reactants are taken into
account together with a single step reaction. The present work does not attempt to extend the model under study with additional details (e.g. [28, 64, 94]) but is mainly concerned with the effect of transport limitations on the flame structure.

Finally, it should be noted that intraparticle gradients related to transport effects can also arise in relation to the regime in which the fixed bed combustion process takes place. All models discussed earlier assume that the conversion takes place in the quasi-homogeneous regime, where it is assumed that the typical size of the reaction zone is much larger than the particle size. However, fixed bed combustion can also occur in the so-called relay-race regime, where the width of the reaction zone is of the same magnitude or smaller than the particle size [95]. A one dimensional analytical model [92] has recently been developed that can be used in this regime. However, at present it cannot account for convective transport of gaseous reactants to the reaction zone. Therefore, its application is limited to combustion synthesis processes and cannot be used to describe reverse combustion. It is not a goal of the present paper to analyze the effect of intraparticle gradients related to the relay-race regime or to adapt the model discussed in this paper to include these effects.

The outline of the paper is as follows. First, a short description of the model equations and its input, a set of physical parameters for a coal bed, are given (Sec. 4.2). Then, numerical solutions to the model equations are presented. (Sec. 4.3). It is shown that these solutions contain two limiting cases, depending on the rate of mass transfer compared to the kinetic rate. After this, the analytical solution to the model equations is introduced and differences with the numerical results are pointed out and explained in terms of the flame structure (Sec. 4.4). This is followed by a short discussion of the results, which contains an error quantification of the analytical solution for a wide range of activation energies and gas velocities (Sec. 4.5). Finally, conclusions are presented (Sec. 4.6).

### 4.2 Model equations and physical parameters

In this section, a short review of the model presented in Ref. [16] will be given. First, the governing equations are discussed in stationary as well as instationary conditions. Results obtained with the instationary version of the model equations will be used to confirm the stationary solution method. Then, an expression for the reaction source term is presented. Finally, data for the transport coefficients and other parameters related to the model are discussed. All data and equations in this section are taken from Ref. [16].

#### 4.2.1 Instationary model equations

The governing equations of the model consist of transport equations for mass, energy and species. Mass conservation is described by continuity equations for the solid material and the gas phase. The continuity equation for the solid fuel is given by

\[
\frac{\partial}{\partial t} ((1 - \epsilon) \rho_s) = -R,
\]  
(4.1)
where $\epsilon$ is the total porosity of the fuel bed, $\rho_s$ the true density of the fuel and $R$ the reaction source term. In writing down this equation, it is assumed that the fuel bed consists of nonporous particles. The porosity is then equal to the volumetric fraction of void space in the bed and the true density of equals the particle density. If the apparent density $\rho_{sa}$ of the fuel bed is defined as the density of the fuel bed including the void space, the porosity can be determined from

$$\epsilon = 1 - \frac{\rho_{sa}}{\rho_s}. \quad (4.2)$$

The continuity equation for the gas phase is given by

$$\frac{\partial}{\partial t} (\epsilon \rho_g) + \frac{\partial}{\partial x} (\epsilon \rho_g v_g) = R. \quad (4.3)$$

Here, $v_g$ is the velocity of the gas. Due to the large amount of inert nitrogen in air, the source term this continuity equation will contribute little to the gas mass flow. This means that the gas mass flow $m_g$ is approximately constant, i.e. the continuity equation for the gas phase (Eq. 4.3) can be replaced by

$$m_g = \rho_g \epsilon v_g \sim m_{gu} = \epsilon_u \rho_{gu} v_{gu}. \quad (4.4)$$

The subscript $u$ indicates that the value of $m_g$ in the unburnt region, far upstream from the flame front. The transport equation for the oxygen mass fraction $Y$ is given by

$$\frac{\partial}{\partial t} (\epsilon \rho_g Y) + \frac{\partial}{\partial x} (\epsilon \rho_g v_g Y) + \frac{\partial}{\partial x} (\epsilon \rho_g v_{gd} Y) = -\omega R, \quad (4.5)$$

where $\omega$ is a mass based stoichiometric coefficient and $v_{gd}$ is the velocity of oxygen relative to the mean flow due to diffusion and dispersion effects. The third term on the left hand side can then be recognized as the derivative of a flux caused by diffusion and dispersion. Here, it is assumed that the flux is dominated by dispersion and we introduce an effective dispersion coefficient $D$. On the basis of a gradient flux assumption, the flux can be written as

$$\epsilon \rho_g v_{gd} Y = -\rho_g D \frac{dY}{dx}. \quad (4.6)$$

Finally, an equation for the temperature is needed. Here, it is assumed that the time scale of the heat exchange between the gas phase and the solid phase as well as the heat-up time of the particles in the bed are smaller than the timescale of the propagation of the reaction front. For a coal bed, where the reaction is limited by mass transfer and not by heat transfer, this is a reasonable assumption [16]. In this case, the solid material is in equilibrium with the gas phase and it is appropriate to use a single temperature $T$:

$$\frac{\partial}{\partial t} \left( (1 - \epsilon) \rho_s c_{ps} + \epsilon \rho_g c_{pg} \right) T + \frac{\partial}{\partial x} \left( \epsilon \rho_g v_g c_{pg} T \right) - \frac{\partial}{\partial x} \left( \Lambda \frac{\partial T}{\partial x} \right) = -\Delta H_r R \quad (4.7)$$

Here, $c_{ps}$ and $c_{pg}$ are the specific heats of the solid and the gas phase, respectively. The effective conductivity is indicated with $\Lambda$. Together with the boundary conditions in the unburnt region ($u$) far upstream from the flame front ($x \rightarrow -\infty$)

$$Y |_u = Y_u, \quad T |_u = T_u \quad (4.8)$$
and the burnt region \((b)\) far downstream from the flame front \((x \rightarrow \infty)\)

\[
\left. \frac{dY}{dx} \right|_b = 0 \quad \left. \frac{dT}{dx} \right|_b = 0.
\]  

(4.9)

the problem is completely defined, provided that suitable initial profiles for the variables are specified that result in a solution with a propagating front. The equations (4.1, 4.5, 4.7), together with the additional definitions and boundary conditions given above constitute the instationary model equations. With these equations, \(\epsilon(x, t)\), \(Y(x, t)\) and \(T(x, t)\) can be obtained as a function of the gas mass flow \(m_{gu}\).

### 4.2.2 Stationary model equations

The combustion wave described by the instationary equations is expected to be confined to a narrow spatial region. Outside this domain, gradients in all quantities are expected to be negligibly small. Furthermore, we consider the special case that the wave travels with a constant velocity \(v_s\) described by stationary solutions in a reference frame attached to the combustion front. To obtain these solutions, the set of equations is transformed from the original reference frame in which the solid is at rest to a reference frame attached to the combustion front. The stationary frame is indicated with \(O\), whereas the moving frame is indicated with \(O'\). The \(x\)-coordinate in the moving frame is indicated with a prime. This results in

\[
[x']_{O'} = [x]_O + v_st,
\]  

(4.10)

where \(v_s\) is the constant wave propagation speed. Using \(v_s = \frac{\partial x'}{\partial t}\), the spatial derivative and the time derivative for a variable \(g\) can be written as

\[
\left[ \frac{\partial g}{\partial x} \right]_O = \left[ \frac{dg}{dx'} \right]_{O'},
\]  

(4.11)

\[
\left[ \frac{\partial g}{\partial t} \right]_O = v_s \left[ \frac{dg}{dx'} \right]_{O'}.
\]  

(4.12)

In this coordinate system a time-independent solution exists, which means that the time derivative that would usually be present in Eq. (4.12) is absent. All instationary terms in the original set of equations become convective terms in the new coordinate system. Leaving out the prime in the \(x\)-coordinate, the model equations in the new system become:

\[
v_s \frac{d}{dx} (\rho_s (1 - \epsilon)) = -R \]  

(4.13)

\[
v_s \frac{d}{dx} (\epsilon \rho_g Y) + \frac{d}{dx} (\epsilon \rho_g v_g Y) - \frac{d}{dx} (\rho_g D \frac{dY}{dx}) = -\omega R
\]  

(4.14)

\[
v_s \frac{d}{dx} ((1 - \epsilon) \rho_s c_{ps} T) + v_s \frac{d}{dx} (\epsilon \rho_g c_{pg} T) + \frac{d}{dx} (\epsilon \rho_g v_g c_{pg} T)
\]  

\[
- \frac{d}{dx} \left( \Lambda \frac{dT}{dx} \right) = -\Delta H_r R
\]  

(4.15)
The boundary conditions in the new system are given at the unburnt side \((x \to -\infty)\) by
\[
\epsilon|_u = \epsilon_u, \quad Y|_u = Y_u, \quad T|_u = T_u \quad (4.16)
\]
and at the burnt side \((x \to \infty)\) by
\[
\frac{dY}{dx}|_b = 0, \quad \frac{dT}{dx}|_b = 0. \quad (4.17)
\]
Instead of the front velocity \(v_s\) the solid mass flow at the unburnt side,
\[
m_{su} = (1 - \epsilon_u)\rho_s v_s. \quad (4.18)
\]
is used to describe the results. The solid mass flow \(m_{su}\) and the gas mass flow \(m_{gu}\) are more convenient parameters to use, because they directly determine the stoichiometry in the reaction zone as well as the conversion rate.

The stationary model equations (4.13,4.14) and (4.15) together with the boundary conditions and additional definitions are more convenient to use for parametric studies, hence the unsteady set. Spatial profiles \(\epsilon(x), Y(x)\) and \(T(x)\) as well as \(m_{su}\) can easily be obtained as a function of gas mass flow \(m_{gu}\).

### 4.2.3 Model data and additional expressions

To solve the model equations, expressions for the reaction source term, the dispersion coefficient and the conductivity coefficient are required. To obtain an expression for the source term \(R\), the heterogeneous surface reaction of coal with oxygen
\[
C + \omega O_2 \rightarrow (1 + \omega) CO_2, \quad (4.19)
\]
is used in the model. As measurements indicate that the primary product in the reaction zone is \(CO_2\) [16], this is a reasonable assumption. An Arrhenius expression for the surface reaction rate of coal particles is given by Field [96]:
\[
R_s = k_r \rho_g Y. \quad (4.20)
\]
Here, \(k_r\) is the rate constant defined by
\[
k_r = A_f T \exp \left( -\frac{E_a}{RT} \right), \quad (4.21)
\]
in which the pre-exponential factor is indicated with \(A_f\) and the activation energy by \(E_a\). To obtain a volumetric reaction rate, the source term \(R\) has to be multiplied with the specific surface area. For spherical particles of diameter \(d_p\) in an SC (simple cubic) structure, the surface area per unit volume before combustion takes place is given by
\[
S_u = \frac{\pi}{d_p}. \quad (4.22)
\]
A shrinking core model is considered to be appropriate to describe the conversion process. As discussed earlier, the particles are considered to be non-porous. Then,
the reaction takes place only at the surface of the spherical core. The particles are not expected to move in the bed: the solid material which has been removed by the reaction is assumed to be replaced by a highly porous ash layer which is considered to be part of the void space in the bed. Under these conditions, the specific surface area per unit volume in the bed is given by [16]

\[ S = S_u \left( \frac{1 - \epsilon}{1 - \epsilon_u} \right)^{2/3}. \]  

(4.23)

The reaction rate per unit volume can then be expressed by

\[ R = R_s S = k_r S_u \left( \frac{1 - \epsilon}{1 - \epsilon_u} \right)^{2/3} \rho_g Y. \]  

(4.24)

In the equations above, it is assumed that kinetics govern the conversion rate of the coal particles in the bed. However, for coal particles the effect of mass transfer of reactants and products through a boundary layer surrounding the particle is important. This can be taken into account by introducing a mass transfer coefficient \( k_m \) in the reaction source term. With the introduction of \( k_m \), the source term then becomes [16, 34]

\[ R = \frac{1}{k_r^{-1} + k_m^{-1}} S_u \left( \frac{1 - \epsilon}{1 - \epsilon_u} \right)^{2/3} \rho_g Y. \]  

(4.25)

It can be seen that in the limit \( k_m \to \infty \), the source term reduces to the expression given in equation (4.24). To determine whether the kinetics or mass transfer effects dominate the source term, the dimensionless mass transfer coefficient \( K_m \) can be introduced:

\[ K_m = \frac{k_m}{k_r}. \]  

(4.26)

If \( K_m \to \infty \), the source term is dominated by kinetics, while \( K_m \to 0 \) indicates that the reaction is controlled by mass transfer effects. Note that \( K_m \) is a function of the temperature, because the mass transfer coefficient and the Arrhenius constant are temperature dependent. Therefore, to characterize the effect of mass transfer limitations in a flame it is convenient to use \( K_{mb} \), i.e. the value of \( K_m \) at the burnt side of the flame where the temperature is maximal.

Finally, expressions for the gas density, the effective conductivity the dispersion coefficient and the mass transfer coefficient are needed. The gas density is given by the ideal gas law at constant pressure

\[ \rho_g = \rho_g u \frac{T_u}{T}. \]  

(4.27)

The effective axial dispersion coefficient for heat conduction is given by [16]

\[ \Lambda = \lambda_{s0} + 0.8 m_{gu} c_{pg} d_p. \]  

(4.28)

where \( \lambda_{s0} \) is the conductivity of the stagnant bed. The second term is the conductivity due to the contribution of the flow. The dispersion coefficient is given by [16]

\[ D = \frac{v_{gu} \epsilon_u d_p}{2}. \]  

(4.29)
4.3 Model Results

### Table 4.1: Physical parameters used for the calculations for a propagating reaction front in a bed of coal particles [16].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_u$</td>
<td>K</td>
<td>288</td>
</tr>
<tr>
<td>$\Delta H_r$</td>
<td>J g$^{-1}$</td>
<td>$-28.9 \times 10^3$</td>
</tr>
<tr>
<td>$c_{ps}$</td>
<td>J g$^{-1}$K$^{-1}$</td>
<td>1.8</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>g cm$^{-3}$</td>
<td>$1220 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\rho_{sa}$</td>
<td>g cm$^{-3}$</td>
<td>$470 \times 10^{-3}$</td>
</tr>
<tr>
<td>$d_p$</td>
<td>cm</td>
<td>2.5</td>
</tr>
<tr>
<td>$\lambda_{a0}$</td>
<td>J cm$^{-1}$s$^{-1}$K$^{-1}$</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\rho_{gu}(T_u)$</td>
<td>g cm$^{-3}$</td>
<td>$1.226 \times 10^{-3}$</td>
</tr>
<tr>
<td>$c_{pg}$</td>
<td>J g$^{-1}$K$^{-1}$</td>
<td>1.13</td>
</tr>
<tr>
<td>$Y_u$</td>
<td>-</td>
<td>0.23</td>
</tr>
<tr>
<td>$A_f$</td>
<td>cm K$^{-1}$s$^{-1}$</td>
<td>$6 \times 10^4$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>kJ mol$^{-1}$</td>
<td>150</td>
</tr>
<tr>
<td>$\omega$</td>
<td>-</td>
<td>2.67</td>
</tr>
</tbody>
</table>

To calculate the mass transfer coefficient $k_m$, the correlation for the Sherwood number, 
\[ \text{Sh} = 2 + 0.81 \epsilon^{-1/2} \text{Re}_p^{1/2} \text{Sc}^{1/3} \quad 0 < \text{Re}_p < 500 \] (4.30) can be used [91]. Here, the Sherwood number Sh (i.e. the dimensionless mass transfer coefficient) is given by
\[ \text{Sh} = \frac{k_m d_p}{D}, \] (4.31)
the particle Reynolds by
\[ \text{Re}_p = \frac{U d_p}{\nu}, \] (4.32)
where $\nu$ is the kinematic viscosity, and the Schmidt number by
\[ \text{Sc} = \frac{\nu}{D}. \] (4.33)

Data for the diffusion coefficient $D$ and the viscosity $\nu$ are obtained from Ref. [97]. The additional expressions presented here together with the instationary and stationary version of the model equations are implemented in the one dimensional laminar flame code Chem1d [98].

## 4.3 Model Results

### 4.3.1 Base case

First, the instationary set of equations is employed for a simulation in which a steady propagating front is subjected to a stepwise increase in the gas mass flow (Fig. 4.2). The instationary effects related to the increase illustrate that the model equations can
The effect of interparticle transport limitations on reverse combustion

Figure 4.2: Effect of a step in the gas mass flow. Fig. (a-c): spatial flame profiles of $Y$, $T$ and $\epsilon$ for $\Delta t = 100$ s. Fig. (d): $m_{su}$ as a function of $t$. At $t = 2.8$ h, $m_{gu}$ is increased from $2.5 \times 10^{-3}$ g cm$^{-2}$s$^{-1}$ to $1.0 \times 10^{-2}$ g cm$^{-2}$s$^{-1}$. At $t = 0$, $x_s = 60$; at $t = 3.5$ h, $x_s = 0$ cm.

deal with this. Furthermore, the solutions shortly before and after application of the step show that stationary solutions in a reference frame attached to the combustion front indeed exist.

At the start of the simulation a gas mass flow of $m_{gu} = 2.5 \times 10^{-3}$ g cm$^{-2}$s$^{-1}$ was applied to the system. Then, the simulation was run for a time interval long enough to diminish any effects of the initial solution in the time interval displayed (cf. Fig. 4.2). At $t = 3.5$ h the mass flow was increased with a factor 4 to $m_{gu} = 1.0 \times 10^{-2}$. In the spatial profiles, the propagation of the front can be seen by a movement of the boundary layers of $Y$ (Fig. 4.2a), $T$ (Fig. 4.2b) and $\epsilon$ (Fig. 4.2c).

The solid mass flow $m_{su}$ (Fig. 4.2d) was determined by using equation 4.18. The velocity $v_s$ in this equation is obtained by tracking the location $x_s$ of the point at which $T = 800$ K. A linear interpolation of the temperature profile is used to determine $x_s$. From the locations $x_s$, the velocity can then be determined by

$$v_s = \frac{\Delta x_s}{\Delta t}$$ (4.34)
For $\Delta x_s$ and $\Delta t$ the results of two subsequent iterations are used, results in $\Delta t = 10\, s$.

From the results, it can be seen that $m_{su}$ is constant in the initial phase of the simulation. When $m_{gu}$ is increased suddenly, the structure of the reaction front needs approximately $0.5\, h$ to adapt to the new conditions. Then, a new stationary structure is formed with a higher $\epsilon$ and $T$ behind the reaction zone and a lower $m_{su}$.

As the instationary simulations indicate that the assumption of a stationary reaction wave structure is justified, the stationary set of equations can be used for further parametric studies. First, the effect of a variation $m_{gu}$ on the flame is studied (cf. Fig. 4.3). The results consist of spatial profiles of $Y$, $\epsilon$, $T$ and the heat release $\dot{q}$. The latter quantity can be determined from the other parameters by the equation

$$
\dot{q} = -\Delta H_r R
$$

and is a measure for the magnitude of the reaction source term. In the profiles, the $x$-coordinate of each flame profile is situated such that $x = 0$ is located at the maximum heat release. In the results, it can be seen that with an increasing mass flow of air, $\dot{q}$ increases. At the same time, the width of the boundary layers in the profiles for $T$ and $Y$ increases. Due to the increased flow of air, the conversion of the solid fuel $\epsilon_b$ as well as $T_b$ become higher. This is in agreement with the instationary results.

The flame parameters $m_{sur}$, $\epsilon_b$, $T_b$ can be determined as a function of $m_{gu}$ (cf. Figs. 4.4a-4.4c). By using $T_b$ in the expression for $K_{mr}$, $K_{mb}$ can also be determined for varying $E_a$ (cf. Fig. 4.4d). It can be observed that $m_{su}$ initially increases when $m_{gu}$ increases, until a maximum is reached. Then, $m_{su}$ decreases until extinction takes place. The temperature $T_b$ increases continuously with $m_{gu}$. The porosity increases also continuously with increasing $m_{gu}$ until it reaches the value one. The dimensionless mass transfer coefficient $K_{mb}$ shows that for low $m_{gu}$, the source term is controlled by kinetics ($K_{mb} > 1$). However, already for $m_{gu} \sim 1.0 \times 10^{-3}\, g\, cm^{-2}\, s^{-1}$ mass transfer effects begin to play a role ($K_{mb} < 1$). Furthermore, the sensitivity of all parameters to small changes in $E_a$ can be seen.

Earlier work (cf. [35, 36]) explains the shape of the curve of $m_{su}$ as a function of $m_{gu}$ (Fig. 4.4a) in terms of two effects resulting from the increasing air flow. The first effect consists of an increase of the reaction rate due to the additional supply of oxygen. This effect is dominant at low $m_{gu}$ and leads initially to an increase of $m_{su}$. The second effect is the additional convective heat transport out of the reaction zone by the increasing gas mass flow. This effect becomes dominant at higher $m_{gu}$ and results in a decrease of $m_{su}$. Extinction of the reaction wave can also be explained in terms of increased convective heat transport. Due to the increased convective transport, the amount of heat needed to sustain the reaction wave increases. To generate this heat, more solid fuel needs to be converted, which leads to an increase of the porosity. At the extinction point, the porosity approaches the value of one. This means that there is no additional solid material left to generate the heat necessary to sustain the front when $m_{gu}$ is increased further: extinction takes place [35, 36].

In the calculations it can be seen that the value $\epsilon = 1$ is not reached exactly. From this observation, it can be concluded that the numerical solutions do not reach the extinction point completely. This is a limitation of the current parametrization in the numerical implementation of the model equations, a well-known problem in
Figure 4.3: Spatial flame profiles for increasing gas mass flow. Results for $Y$, $T$, $\epsilon$ and $\dot{q}$ for $m_{gu} = (0.4 : 0.4 : 2.0) \times 10^{-2}$ g cm$^{-2}$s$^{-1}$. 
4.3 Model Results

Figure 4.4: Flame parameters as a function of $m_{gu}$ for different $E_a$. Results for $m_{su}$, $\epsilon_u$, $T_b$ and $K_{mb}$. Solid line: $E_a = 150 \text{ kJ mol}^{-1}$, dashed line: $E_a = 160 \text{ kJ mol}^{-1}$, dotted line: $E_a = 170 \text{ kJ mol}^{-1}$. Line S: limiting value for stoichiometric combustion.
the combustion literature. Solutions to this type of problem can be implemented [99, 100], but as the exact values of the extinction limit are not of interest in the present work, this is not improved here. To illustrate that the region of the solution near the extinction point that is not covered is small, additional limiting values for \( m_{su} \) and \( T_b \) can be determined and compared to the numerical results. The limiting value for the solid mass flow \( m_{su,S} \) is determined by the stoichiometry ratio of solid and gas. It can be derived from global conservation of mass of the gas and solid reactants (cf. appendix A) and is expressed by:

\[
m_{su,S} = \frac{Y_u}{\omega} m_{gu,S}.
\] (4.36)

A more detailed expression of this equation is presented in the appendix. Similarly, an expression for the limiting value of the temperature can be obtained (cf. appendix A):

\[
T_{b,S} = T_u \left( \frac{Y_u c_p s}{\omega c_{pg}} + 1 \right) - \frac{Y_u \Delta H_r}{\omega c_{pg}}
\] (4.37)

In the results for \( m_{su} \) (Fig. 4.4a) and \( T_b \) (Fig. 4.4c), it can be seen that the limiting values are indeed almost reached.

### 4.3.2 Transport limitations

To investigate the consequences of mass transport limitations, calculations were performed for the kinetically controlled case \( K_{mb} \to \infty \) and the mass transport limited case \( K_{mb} \to 0 \) (Fig. 4.5). To study these cases, parameters in the model equations have to be changed. In the first case, \( k_m \to \infty \). In the second case, \( \Delta H_r = -60 \times 10^4 \text{ J g}^{-1} \). Here, \( \Delta H_r \) is chosen, because it can be shown with integral conservation equations for the oxygen mass fraction and the temperature increase of this parameter leads to an immediate increase of the temperature at the burnt side under all conditions. Due to the Arrhenius constant in the expression for \( k_r \) (cf. Eq. 4.21) the increase of the directly to an increase of \( K_{mb} \) (cf. eqn. 4.26). To rule out the effect of temperature variations in \( K_{mb} \) via \( k_m \) (the parameters \( \nu \) and \( D \) are temperature-dependent), \( k_m \) is kept at a constant value of \( 7.8 \text{ cm s}^{-1} \). Because of the parameter changes in the calculations, the obtained results will deviate significantly from observations in practical combustion furnaces. However, these changes are justified when keeping in mind the purpose of giving a clear representation of limiting cases of the combustion process.

The results of the calculations (Fig. 4.5) indicate that the flame structures are different for the two limiting cases. The flame with \( K_{mb} \to \infty \) has a source term which is not limited by mass transfer effects (Fig. 4.5c). The flame consists of a preheat zone and a reaction zone. In the preheat zone, the temperature is increasing, but \( \dot{q} \) is still negligibly small. In the reaction zone, \( \dot{q} \) reaches its maximum. This structure is caused by the exponential dependence of \( R \) on \( T \), which causes it to be exponentially large in the reaction zone (where \( T \sim T_b \)) compared to the preheat zone (where \( T \ll T_b \)). This flame structure is well known and closely resembles the structure of gaseous premixed flames (cf. [101]).
4.3 Model Results

Figure 4.5: Spatial flame profiles of $Y$ and $\epsilon$ (upper figures) and $T$ and $\dot{q}$ (lower figures) for two limiting cases of $K_{mb}$. Results for $K_{mb} \to \infty$ (left figures; conditions: $k_m \to \infty$, $m_{gu} = 1.9 \text{ g cm}^{-2}\text{s}^{-1}$) and $K_{mb} \to 0$ (right figures; conditions: $k_m = 20 \text{ cm s}^{-1}$, $K_{mb} = 2.2 \times 10^{-6}$, $m_{gu} = 1.8 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$, $\Delta H_r = -60 \times 10^4 \text{ J g}^{-1}$)

(a) (b) (c) (d)
The flame with $K_m \rightarrow 0$ has a source term that is dominated in almost the entire flame structure by mass transfer (Fig. 4.5d). The flame starts with a very thin reaction controlled layer. Here, the temperature is moderate, which means that $k_r \leq k_m$ (i.e. $K_m \geq 1$). However, the exponential dependence of the source term on the temperature causes the temperature to increase rapidly. At the location where $k_r = k_m$ (i.e. $K_m = 1$), the mass transfer controlled layer starts. Here, the mass transfer process limits the magnitude of the source term. The consumption rate of the incoming oxygen flow is inhibited, which causes an increase of the boundary layer size of $Y$ (Fig. 4.5b). The limitation results in a gradual decrease of the source term over a long distance (Fig. 4.5c). Thus, the diminished exponential dependence of $R$ on $T$ in the region downstream of the maximum of $\dot{q}$ gives rise to a reaction wave which is thicker than for the kinetically controlled case and which has its maximum at the upstream part of the wave instead of at the downstream part.

4.4 Comparison with analytical solutions

4.4.1 The analytical solution

In the following parts of this paper, the numerical results will be compared to the analytical solution presented in Ref. [16]. In this section, a short recapitulation of the analytical solution procedure and its results is given. The first step of the solution procedure consists of the introduction of two assumptions in the original set of stationary equations (cf. eqs. 4.13, 4.14, 4.15). With additional annotations (a star and an accent), this set can be written as:

\begin{align}
    v_s \frac{d}{dx} \left( \rho_s (1 - \epsilon') \right) &= -R, \\
    v_s \frac{d}{dx} \left( \epsilon \rho_g Y^* \right) + \frac{d}{dx} \left( \epsilon \rho_g v_g Y \right) - \frac{d}{dx} \left( \rho_g D \frac{dY}{dx} \right) &= -\omega R, \\
    v_s \frac{d}{dx} \left( (1 - \epsilon) \rho_s c_p s T \right) + v_s d \frac{d}{dx} \left( \epsilon \rho_g c_p g \right)^* + \frac{d}{dx} \left( \epsilon \rho_g v_g c_p g T \right) - \frac{d}{dx} \left( \Lambda \frac{dT}{dx} \right) &= -\Delta H_r R.
\end{align}

The first assumption consists of

$$v_s \ll v_g$$

which means that the the convective terms indicated with a star in eqns. (4.38, 4.39) can be neglected. This assumption holds in good approximation for reverse combustion conditions of a coal fuel layer and can be supported by a non-dimensional analysis (cf. Ref. [16]). The other assumption is connected to the porosity in the temperature equation (eqn.(4.40)) indicated with a prime, which is kept at a constant value $\epsilon_u$, i.e.

$$\epsilon = \epsilon_u$$

This is an approximation that is introduced to facilitate the numerical solution procedure and is not based on physical reasoning. The effect of both assumptions was
investigated with numerical calculations. Results obtained without the convective terms indicate that their effect is limited to errors smaller than 1% in $\epsilon_b$, $T_b$ and $m_{gu}$. However, the effect of the second assumption can lead to errors of 50% in $m_{su}$ (cf. Fig. 4.6). The deviations become larger with growing $m_{gu}$ as the porosity starts to deviate increasingly from $\epsilon_u$.

The second step of the solution procedure consists of employing the method of matched asymptotic expansions [102]. In this method, the model equations are nondimensionalized. This leads to the introduction of the definition of the dimensionless inverse of the activation energy $\gamma$:

$$\gamma = \frac{RT_b^2}{E_a(T_b - T_u)}$$

(4.43)

Due to the largeness of the activation energy, $\gamma \ll 1$. All dimensionless variables $\xi$ are expanded in a series of $\gamma$, i.e.

$$\xi = \xi_0 + \xi_1 \gamma + \xi_2 \gamma^2 + \ldots$$

(4.44)

Then, it is assumed that the flame structure is kinetically controlled (cf. Figs. 4.5a, 4.5c) and separate sets of equations are written for the preheat zone, where the reaction source term is negligible, and the reaction zone, where it is dominant. The series are substituted in the sets of equations and solutions for each zone are obtained for the lowest-order terms in the series. By matching the solutions in both domains (cf. [102]), i.e. by expressing mathematically that the solutions in the two domains have a smooth transition, expressions for the mass burning rates and the spatial profiles of the variables are obtained.
The third step of the solution procedure consists of redimensionalizing the obtained solution. This leads to a final set of equations [34] used in the present work. The first of these equations consists of the dimensionless convective energy flux \( \phi \)

\[
\phi = \frac{m_{gu}c_{pg} + m_{su}c_{ps}}{\kappa_r},
\]

(4.45)

where the scaling constant \( \kappa_r \) is given by

\[
\kappa_r = \left( -\frac{\Delta H_r}{T_b - T_u} S_u \left( \frac{\epsilon_b - \epsilon_u}{1 - \epsilon_u} \right)^{2/3} \times \right.
\]

\[
\left. \frac{\rho_uT_u}{T_b} (Y_u - Y_b) \frac{Le_g k_{r,b}}{1 + K_{mb}} \gamma^2 \right)^{1/2}
\]

(4.46)

Here, the Lewis number is defined by

\[
Le_g = \frac{\Lambda m_{gu}}{\rho_g (m_{gu}c_{pg} + m_{su}c_{ps}) D},
\]

(4.47)

and \( k_{r,b} \) is the Arrhenius rate constant (Eq. (4.21)) evaluated at \( T_b \). The second equation is an expression for the dimensionless convective energy flux, resulting from the matching procedure,

\[
(1 + K_{mb}) \int_0^{\infty} \frac{(\alpha + \eta) e^{-\eta}}{e^{-\eta} + K_{mb}} d\eta = \frac{3}{4} \phi^2
\]

(4.48)

where the stoichiometry parameter related to the solid phase \( \alpha \) is defined by

\[
\alpha = \frac{1 - \epsilon_b - \epsilon_u}{\phi}.
\]

(4.49)

The third and fourth equations are the integral equations for conservation of mass and energy:

\[
m_{gu} \frac{Y_u - Y_b}{\omega} = m_{su} \left( \frac{\epsilon_b - \epsilon_u}{1 - \epsilon_u} \right),
\]

(4.50)

\[
m_{gu} \frac{Y_u - Y_b}{\omega} = \frac{m_{gu}c_{pg} + m_{su}c_{ps}}{(-\Delta H_r)} (T_b - T_u).
\]

(4.51)

Equations (4.43) to (4.51) contain a solution for \( \epsilon_b, m_{gu} \), and \( T_b \) which is accurate up to first order in \( \gamma \). More explicit expressions for these variables are not obtained, which means that the full solution has to be determined by solving this set numerically.

A comparison between the numerical and analytical solutions, both for the set of eqs. (4.13, 4.14, 4.15) together with the assumptions given by eqn. (4.41, 4.42) shows that for small \( m_{gu} \) the curves for \( m_{su} \) (Fig. 4.7a) and \( T_b \) (Fig. 4.7b) coincide. However, at larger \( m_{gu} \) (\( m_{gu} \sim 0.25 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1} \)) the analytical solutions start to deviate. The most logical explanation for this is the increase of \( \gamma \) (cf. Fig. 4.7c), causing a larger contribution of the higher order terms in the asymptotic series (cf. Eq. 4.44) that are not represented in the analytical solution. The increase of the
4.4 Comparison with analytical solutions

Figure 4.7: Analytical solution versus numerical solution for $m_{su}$, $T_b$, $\gamma$ and $K_{mb}$ as a function of $m_{su}$. Line S: limiting values for stoichiometric combustion.

errors in $m_{su}$ and $T_b$ with increasing in $\gamma$ (cf. Fig. 4.7b) supports this reasoning. The dependence of the accuracy of the solution on the perturbation parameter is well a known property of this type of solutions and can be mended by including higher order terms in the solution procedure (cf. [101, 102]). However, results for $K_{mb}$ (Fig. 4.7d) indicate that the flame structure is shifting towards the mass transfer controlled limit with increasing $m_{gu}$. This violates the assumption that the flame structure is kinetically controlled and may also contribute to the deviations of $m_{su}$ and $T_b$. Thus, the presence of mass transfer effects leads to a more complex behavior of the analytical solution than is generally observed in case of using purely kinetic source terms.

4.4.2 Limit of high activation energy

In order to investigate the individual contributions of the finite value of $E_a$ (represented by $\gamma$) and the deviations of the kinetically controlled flame structure (represented by $K_{mb}$) in the observed error, the limit of high activation energy is explored. An increase of the activation energy reduces the magnitude of the higher
order terms in the asymptotic series, which means that the analytical solution (eqs. (4.43) to (4.51)) will approach the numerical solution. The effect of $\gamma$ is then nullified, while the error related to $K_{mb}$ can still be observed.

Exploring $E_a \to \infty$ brings about the difficulty that the solution will change when the activation energy is varied. For small changes in the activation energy, the changes in $m_{su}$ will also be relatively small (cf. Fig. 4.4). However, to explore $E_a \to \infty$, changes in $E_a$ of more than an order of magnitude are required, which leads to large variations in $m_{su}$. This makes it difficult to monitor the error in the prediction of $m_{su}$. An additional difficulty is that the effect of mass transfer limitations on the flame structure will vary. The parameter $K_{mb}$ will change due to the changes in the Arrhenius rate constant (cf. Eq. 4.21), while this is a parameter that needs to be kept constant.

To explore $E_a \to \infty$ without the associated difficulties, a scaling procedure is applied based on the analytical solution. In this solution, the activation energy is only present in the scaling constant $\kappa_r$ in Eq. (4.46). If $\kappa_r$ can be kept at the same value while varying $E_a$, the model results remain also at a constant value. The condition

$$\kappa_r = \kappa_{r0},$$

(4.52)

where the subscript 0 stands for the original value of $\kappa_r$, can be met if

$$Le_k \frac{k_{rb}K_{mb}}{1 + K_{mb}} \gamma^2 = \text{constant}$$

(4.53)

Furthermore, to ensure that the effect of mass transfer limitations is kept constant, the condition

$$K_{mb} = K_{mb0}$$

(4.54)

has to be fulfilled. Both conditions are met if

$$\frac{\gamma^2}{D} = \frac{\gamma_0^2}{D_0}$$

(4.55)

and

$$k_{rb} = k_{rb0}$$

(4.56)

In order to obtain this result, the dispersion coefficient and the pre-exponential can be scaled by

$$D = D_0 \left(\frac{E_{a0}}{E_a}\right)^2,$$

(4.57)

$$A_f = A_{f0} e^{-\frac{E_{a0} - E_a}{m_b}}.$$  

(4.58)

respectively. Now, variations in $\gamma$ are compensated by adaption of the diffusion coefficient. Variations of the exponential factor are compensated by a change in the pre-exponential factor.

Numerical solutions for the limit $E_a \to \infty$ of the scaled problem at constant $m_{su}$ show that without the effect of mass transfer limitations ($k_m \to \infty$; Fig. 4.8a) the analytical solution stays constant. The increase of the activation energy initially
leads to a short interval in \( \gamma \) where the numerical solution deviates further from the analytical solution, but already at \( \gamma = 2 \times 10^{-2} \) the solutions start to converge. Note that the scaled numerical solutions vary as a function of \( E_a \), because the scaling procedure is based on a first order result in \( \gamma \). This means that the scaling becomes correct in the limit \( E_a \to \infty \) only.

For the case \( k_m = 20 \text{ cm s}^{-1} \), the scaled numerical solution does not approach the analytical solution in the studied parameter range. The solutions for \( m_{su} \) as a function of the gas mass flow \( m_{gu} \) give a similar result (figure 4.9). For the case \( k_m \to \infty \) (cf. Figs. 4.9a, 4.9c), the correct limit is obtained, while for the case \( k_m = 20 \text{ cm s}^{-1} \) no convergence takes place (cf. Figs. 4.9b, 4.9d).

In the results, it can be observed that not all scaled numerical solution reach the stoichiometric limit (Fig. 4.9a). This is a limitation of the scaling procedure. Only for values of \( m_{gu} \) where the analytical solution exists, a scaling factor can be determined. Therefore, scaled numerical solutions only exist in the \( m_{gu} \)-range where also an analytical solution exists.

The results presented in this section for \( k_m = 20 \text{ cm s}^{-1} \) (Figs. 4.9b, 4.9d) give strong indications that for \( E_a \to \infty \), analytical solutions and scaled numerical solutions do not converge when mass transfer limitations play a role. However, from the results for \( k_m \to \infty \) (Fig. 4.9a) it can be seen that it is normal for the scaled numerical solution to show diverging behavior initially, while convergence takes place in a later stage. This means that also the results for \( k_m = 20 \text{ cm s}^{-1} \) may still converge if \( \gamma \) is increased further. Thus, more information is necessary to obtain certainty about the asymptotic behavior of this case.

Spatial profiles of the flames can be used to draw definitive conclusions about the diverging behavior of the mass transfer limited case. First, we consider spatial profiles of the kinetically limited case, i.e. \( [E_a \to \infty, k_m \to \infty] \) (Figs. 4.11a, 4.11b). These results indicate that the spatial profile of \( Y \) and \( \dot{q} \) show the behavior expected.
Figure 4.9: Limit of high activation energy: $m_{su}$ and $\gamma$ as a function $E_a$. N and A: numerical and analytical solution at $E_a = 150$ kJ mol$^{-1}$. Left: $k_m \to \infty$. Curves I to III: scaled numerical solutions for $E_a = 200$ kJ mol$^{-1}$, 1.0 MJ mol$^{-1}$, 10.0 MJ mol$^{-1}$. Right: $k_m = 20$ cm s$^{-1}$. Curves I to III: scaled numerical solutions for $E_a = 200$ kJ mol$^{-1}$, 1.0 MJ mol$^{-1}$, 8.0 MJ mol$^{-1}$. S: limiting values for stoichiometric combustion.
4.4 Comparison with analytical solutions

Figure 4.10: Limit of high activation energy for $T_b$ and $K_{mb}$ as a function of $m_{gu}$ for the case $k_m = 20$ cm s$^{-1}$. A: analytical solution, N: numerical solution. Curves I to III: scaled numerical solutions for $E_a = 200$ kJ mol$^{-1}$, 1.0 MJ mol$^{-1}$, 8.0 MJ mol$^{-1}$. S: temperature for stoichiometric combustion.

from the scaling procedure. The boundary layer of $Y$ decreases, which is in agreement with the decrease of the diffusion coefficient due to the scaling procedure (cf. Eq. 4.57). Furthermore, due to an increase of the activation energy, $\dot{q}$ is confined to a more narrow region, which leads to an increased separation of the reaction zone and the preheat zone. For the mass transfer limited case, i.e. $[E_a \to \infty, k_m = 20$ cm s$^{-1}]$, the results are different. It can be seen that the part of the boundary layer of $Y$ in front of the reaction zone disappears (cf. Fig. 4.11b, Fig. 4.11d), i.e. the reaction zone shifts to the front of the flame. In addition, the downstream part of the source term extends over a longer distance. This indicates that the flame shifts towards the mass transfer controlled limit despite the precautions taken in the scaling procedure. This is confirmed by results for $K_{mb}$ (Fig. 4.10b), which is decreasing with increasing $E_a$ due to incorrect predictions of the temperature (cf. Fig. 4.10a).

Results for the case $[E_a \to \infty, k_m = 20$ cm s$^{-1}]$ for $m_{su}$ as a function of $m_{gu}$ (Fig 4.9b) supplemented with the spatial profiles (Figs. 4.11a, 4.11b) lead to the conclusion that the scaling procedure does function well for mass transfer limited flames. This entails that the quality of the representation of mass transfer effects in the analytical solution is not sufficient. The model predicts correctly the trend that $m_{su}$ decreases considerably due to the effect of mass transfer, if unscaled results are compared for the case $k_m \to \infty$ (Fig. 4.9a) and (Fig. 4.9b). However, the analysis presented here shows that care should be taken with quantitative predictions.

4.4.3 Validity range of the analytical model

Due to the inaccuracies in the predictions of the analytical solution, it is advisable to make an error quantification with with the aid of numerical calculations if it is used. Here, an example of an error quantification is given. To determine the error
The effect of interparticle transport limitations on reverse combustion

Figure 4.11: Limit of high activation energy: spatial profiles of $Y$ and $\dot{q}$ for different $E_a$. Left: $k_m \to \infty$, scaled numerical solutions for $E_a = 200$ kJ mol$^{-1}$, 1.0 MJ mol$^{-1}$, 10.0 MJ mol$^{-1}$. Right: $k_m = 20$ cm s$^{-1}$, scaled numerical solutions for $E_a = 200$ kJ mol$^{-1}$, 1.0 MJ mol$^{-1}$, 8.0 MJ mol$^{-1}$. 
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in the analytical model calculations are performed in the parameter range consisting of variations of $m_{gu}$ from $2.5 \times 10^{-4}$ up to the extinction point of the flame. The calculations were repeated for activation energies ranging from $150 \text{ kJ mol}^{-1}$ to $6.3 \text{ MJ mol}^{-1}$. In the $(m_{gu}, E_a)$-domain studied, the error was determined by

$$\Delta = \left| \frac{m_{su,N} - m_{su,A}}{m_{su,A}} \right|. \quad (4.59)$$

The results (Fig. 4.12) consists isolines of the error in the studied domain, of which the boundaries are indicated with a thick black line. These boundaries correspond to the studied parameter range. The results indicate that the error increases rapidly when $E_a$ and $m_{gu}$ increase. The error is larger than 0.20 for $[E_a \geq 1 \text{ MJ mol}^{-1}, m_{gu} \geq 0.3]$ and reaches values over 0.6 near the values of $m_{gu}$ where the flame extinguishes.

The same data set can be used to present $\Delta$ as a function of the parameters $\gamma$ and $K_{mb}$. Results are presented in Fig. 4.13. Here, the upper and lower boundaries of the domain are determined by simulations with $E_a = 150 \text{ J mol}^{-1}$ and $E_a = 6.3 \text{ MJ mol}^{-1}$ respectively. The right boundary is determined by the minimum value of $m_{gu}$, i.e. $m_{gu} = 2.5 \times 10^{-4}$. The left boundary is given by the extinction limits of the flame. All boundaries are indicated with thick black lines. The results indicates that the analytical model becomes increasingly inaccurate for increasing $\gamma$ and decreasing $K_{mb}$ in the larger part of the domain. Only for high values of $K_{mb}$ this is not the case.
4.5 Discussion

In the work presented here, it is shown that mass transfer effects play an important role for the reverse combustion of coal (cf. Fig. 4.4). When the effect of mass transfer is large, the flame structure starts to deviate considerably from a flame structure controlled by kinetics. (cf. Fig. 4.5c). The flame structure no longer consists of a distinct preheat zone and reaction zone. Instead, an elongated reaction zone is formed in which the maximum of the source term is situated at the upstream part of the flame (cf. Fig. 4.5d).

By making use of a model that can be solved analytically, concessions have to be made to the level of complexity. All assumptions made in the model can be considered as sources of errors. For example, the assumption \( m_g \sim m_{gu} \) (cf. Eq. 4.4) leads to errors of order \( \frac{Y_u}{m_{gu}} \) in \( m_{gu} \), which will have an effect of similar magnitude on the results. Despite these errors, the model results give reasonable predictions and give a clear image of the structure of the flame.

The analytical solution to the model equations involves additional approximations that lead to more sources of error. Firstly, additional assumptions are made to the instationary set of equations (cf. Sec. 4.4.1), of which the constant porosity assumption gives rise to the largest errors (cf. Fig. 4.6). Another error is introduced by the solution method, in which higher order terms in \( \gamma \) are neglected (cf. Fig. 4.9a). Then, there is an error related to the effect of mass transfer on the structure of the flame (cf. Fig. 4.9b), which is not accounted for in the analytical solution method.

The error related to \( K_{mb} \) is the most important one of all errors related to the analytical solution procedure. The analytical solution is explicitly proposed to describe flames with mass transfer limitations and therefore should be usable to predict these effects and to give more insight in the physics of this type of flames. At present, the
solution provides effectively only the qualitative prediction that $m_{sv}$ decreases with decreasing $k_{mb}$. The description of mass transfer effects is only correct for very large values of $k_{mb}$ (i.e. in the limit $k_{mb} \to \infty$) but then, the role of mass transfer can be neglected.

The fact that the error in the analytical solution due to mass transfer effects is a drawback of the model, but a more important objection is the lack of a method to quantify this error or to reduce it. In comparison, the error in the analytical solution for the case $K_{mb} \to \infty$ related to the finite value of $E_a$ can be lowered by including higher order terms in the solution procedure. Furthermore, from the asymptotic series it can be derived that the magnitude of the error in $m_{gu}$ is of the order of $\gamma$, which is an a priori estimate. The use of an asymptotic series ensures that either in the limit of high activation energy or when including a larger number of terms in the asymptotic series, the accurateness of the functional dependence of the solution on $E_a$ becomes in principle as good as desired. In contrast, the functional dependence of the model results on $K_{mb}$ leads to errors even for moderate values of $K_{mb}$.

The numerical solutions offer a good alternative for the analytical solutions. They predict the flame structure correctly and are not dependent of any a priori assumptions of the flame structure. Therefore, solving the model equations numerically is the preferred method. If it is still desired to apply the analytical solution, the numerical calculations offer the possibility to make error quantifications (cf. Fig. 4.12, 4.13) to obtain reliable results.

4.6 Conclusions

In this paper, numerical and analytical solutions to an existing model presented in the literature to describe the combustion process in a fixed bed. At present, this is the only model that both attempts to describe the effect of transport limitations and has been solved analytically. From numerical solutions to the model equations it was observed that the model can indeed successfully describe two limiting cases: the kinetically limited case, with a preheat zone followed by a thin reaction zone, and the mass transfer limited case, with a thin kinetically controlled reaction zone, followed by a thick mass transfer controlled reaction zone.

A comparison of the numerical solutions to the analytical solutions shows that obtaining accurate analytical solutions is more troublesome. The investigation of the analytical solution method has been performed by exploring the limit of high activation energy, together with a scaling procedure. Results show that for flames with mass transfer limitations the analytical and numerical solutions do not converge towards each other. Furthermore, the results show convincingly that this is not only related to the finite value of the activation energy, but also strongly depends on the structure of flames with mass transfer limitations. Because the flame structure is not a priori known, numerical calculations are shown to be essential to estimate the error made in the analytical solution procedure. The numerical analysis presented here proves therefore to be a necessary addition to the analytical solutions.

The data set employed to obtain the results indicates that mass transfer effects discussed in this paper play a role in practical combustion systems for coal. Further-
more, limitation effects can play an important role in other fixed bed combustion processes, e.g. for wood particles. It is now shown that for all these cases care has to be taken with using the present state of the art analytical solutions based on activation energy asymptotics. Instead, even when using more simple models to obtain insight in flame phenomena, numerical modeling is the preferred method.

At present, the analytical model does not give sufficient insight in the functional dependence of reaction wave velocities and temperatures as a function of model parameters for mass transfer controlled flames. However, part of this insight can already be obtained from the spatial profiles presented in this work. The development of an improved analytical solution method for mass transfer controlled flames could add to this. The flame structures presented in this work could be helpful in this process.

In the near future, the work presented in this paper will be extended in two directions. Firstly, the possibility of obtaining analytical solutions for mass transfer controlled flames will be investigated further. Secondly, the numerical model presented here will be adapted to describe the reverse combustion process in more detail to serve as a submodel for the primary combustion zone in a grate furnace. Adding more complex chemistry to the model will be an important next step. As the laminar flame code in which this model is embedded is dedicated to make use of detailed reaction mechanisms, this will be a logical next step.
Chapter 5

The effect of heat losses in reverse combustion experiments

5.1 Introduction

Grate furnace combustion is a widely used conversion method to obtain heat and power from biomass. In the Scandinavian countries and Austria, several hundreds of these plants exist [13, 15]. In order to keep the emissions of these furnaces within the appropriate limits, the design and operating conditions of the furnace need to be optimized. Computational Fluid Dynamics (CFD) has proven to be a cost-effective method of optimizing the energy output of grate furnace combustion [19] and can be used to predict the exhaust gas composition. [21, 22].

An important part of an overall CFD furnace is the description of the solid fuel conversion process on the grate. This is a reverse combustion process because it consists of a reaction front propagating in the opposed direction of the air that flows through the solid fuel layer. An important parameter that characterizes the conversion process is the velocity of the reaction front. The quality of a reverse combustion model depends therefore strongly on the accuracy of the prediction of this parameter. The accuracy can be tested with validation experiments in a laboratory reactor. However, in a laboratory reactor the combustion process can be affected heat transport out of the reaction zone to the environment. Due to the smaller dimensions of a laboratory scale fixed bed reactor, the effect of heat loss is potentially more important than in a grate furnace. This study contains therefore an analysis of the magnitude of this effect.

The front velocity is chosen to quantify the effect of heat losses on the conversion process because:

- **It can be determined easily**
  
The front velocity can be determined easily in a laboratory reactor, because it can be determined from thermocouples mounted at various heights in the fuel layer. The thermocouple signal indicates at which time the front passes the thermocouple. From the time difference and the distance between two thermocouples, the front velocity can be calculated.

- **It is sensitive to fuel parameters and operating conditions**
The sensitivity of the front velocity to the fuel parameters and operating conditions is firmly established by a large number of experimental studies with different fuels and variation of operating conditions like the air flow rate, temperature and oxygen content (although deviations due to heat losses are not accounted for in these studies). Furthermore, a large number of parameters related to the fuel and operating conditions (e.g. specific heat, conductivity, air temperature) is present in analytical expressions for the velocity of the conversion front \[35,103\] as well as in the equations of more detailed numerical models (cf. e.g. \[16,30,60\]).

- **It is strongly related to other conversion process parameters**
  The front velocity is directly related to other combustion processes because when the air flow is kept fixed, it determines the stoichiometry of the conversion process as it represents the amount of solid fuel that reacts with the incoming air flow. In turn, the stoichiometry determines the adiabatic temperature of the conversion process and the gas phase composition (cf. e.g. \[16,30,60\]).

- **It is potentially important for prediction of NO\(_x\) emissions**
  The potential importance for NO\(_x\) predictions stems from the fact that the front velocity and the local temperature determine the heating rate, which affects the release of nitrogen present in the solid fuel in the form of NH\(_3\), HCN, part of which is converted into NO.

- **It is of practical importance for the design and operation of grate furnaces**
  The capacity of the grate furnace is proportional to the height of the fuel layer. At a certain front velocity, determined by operating conditions and fuel properties, the height is directly related to the burnout time. If the design condition is to achieve complete burnout exactly at the end of the grate, the burnout time determines the velocity (operating condition) and length (design parameter) of the grate.

Apart from the general importance of accurate determination of the velocity of the reaction front, three more specific reasons exist to get more control of the experimental error in reverse fixed bed combustion experiments:

1. **Analysis of fuel properties that have a small effect on the front velocity**
   Experimental studies currently cannot be used to investigate the effect of model properties that have a small effect on the front velocity. An example of such a parameter is the effect of particle size. In Refs. \[16,61\] it is concluded that an increasing particle size in the range 10-30 mm results in an increase of the front velocity of 20% On the other hand, in Refs. \[94,104\] it is reported that the front velocity increases when the particle size decreases. An optimized and standardized reactor design on the basis of sound studies will contribute to ending such debates.

2. **Analysis of advanced conversion models**
   Currently, the most advanced model uses a 2-D particle model and predicts front velocities which leads a 10% difference with more simple models \[40\].
However, an analysis in which the predictions of the front velocity for this model together with predictions of other less advanced models were compared to existing data \([16, 57, 61]\) shows that all model results fall within the experimental error.

3. **Reduction of required fuel batch**

Reduction of the dimensions of a fixed bed reactor leads to a larger effect of heat losses. On the other hand, reduced dimensions lead to less fuel consumption. Reduced batches of fuel allow a better preparation of the fuel, which results in a more homogeneous and better specified fuel, leading to better experimental results. Furthermore, it reduces the time an experiment takes and the reduced amount of fuel leads to less costs.

The laboratory reactor used in most studies to determine the front velocity is a fixed bed reactor (cf. e.g. \([16, 27, 31, 60, 104]\)). It essentially consists of a cylindrical tube filled with fuel particles while air is supplied at the bottom of the layer. The conversion process is started by igniting the fuel layer at the top. The advantage of using such a reactor is that it is much smaller than a grate furnace, while the conversion process is highly similar. However, a disadvantage of using such a reactor consists due to heat losses to the environment. It has already been shown that heat losses to the environment due to imperfect insulation can lead to considerable decreases in the front velocity \([16, 35]\).

In this chapter, we employ a broader definition of heat losses than generally used. Heat losses are here defined as all processes that transport heat out of the reaction zone to elsewhere. By using this definition, heat losses pertain to 1) heat transport to the environment of the reactor, (2) heating of the reactor walls and (3) preheating of the unburnt fuel via the reactor walls. The effect of processes (2) and (3) on the front velocity in a reverse combustion experiment has not been studied yet.

Reverse combustion in the presence of heat losses involves two dimensions: the reaction front propagates in the axial direction of the reactor, while heat transfer to the environment takes place in the radial direction. However, most reverse combustion models are 1-dimensional (cf. e.g. \([16, 26–30]\)). This means that for a comparison between model results and experimental results two methods can be followed. Firstly, the 1-D models can be extended to account for heat losses, e.g. by including an effective 1-D heat loss term or by extending the number of dimensions to two for a full description of heat losses. Secondly, the design of the experimental reactor can be adapted to approximate a 1-D situation as well as possible, for example by insulating the reactor thoroughly.

The models that use an effective 1-D heat loss term \([16, 30]\) do not give a solid analysis of the accuracy of this approach. In Ref. \([16]\) the effective heat loss term is used to describe heat losses to the environment. The effect of the heat loss term on the front velocity is investigated, but a comparison of the 1-D approximation to 2-D results is not presented. Furthermore, the effect of reactor properties (insulating layer, reactor diameter, reactor wall) is not studied. In Ref. \([30]\), the heat loss term represents instationary heating of the reactor walls. However, the effect of this term on the model results is not studied or quantified.
The wide range of variation in the design of experimental setups for fixed bed experiments (Tab. 5.1) shows that there is no general agreement on an optimal reactor design. Although the reactor designs generally seem to be aimed to reduce the effect of heat losses (most reactors have some form of insulation) there is a wide range in reactor cross-section (r = 6-25.5 cm) and in thickness and material of the insulating layer. Furthermore, the reactor used in Ref. [16] seems to be the only one specially adapted to reduce the preheating effect by applying a thin layer of ceramic fibre on the inside of the reactor. In none of the studies that use the reactors described in Tab. 5.1 the reactor design is supported by a quantitative analysis.

It is the goal of this chapter to investigate if the effect of heat losses should be accounted for in 1-D models or should be reduced in the experimental setups. The analysis consists of two parts. In the first part, an experimental identification of the three heat loss mechanisms is performed. The effect of heat losses to the environment is studied by using an insulated and a non-insulated reactor, while the effect of instationary heating of the reactor wall and conduction of heat to the unburnt fuel is studied by using reactor walls with different thermal properties (heat capacity, thermal conductivity). In the second part of the study, we present results of 1-D and 2-D numerical simulations of the reverse conversion process. The purpose of the 1-D simulations is to investigate whether heat losses can be accounted for in 1-D model. The purpose of the 2-D simulations is to investigate if the heat losses can be minimized in the experiments by adapting the reactor design (for example by adjusting the reactor radius).

The numerical model that is used here is a general reverse combustion model. There are three advantages related to the use of this model. Firstly, it has successfully been used in previous studies to describe the propagation of a reaction front in a fuel layer of coal particles. Secondly, a numerical analysis of this model (cf. 4, [1]) showed that it is capable of taking into account interparticle mass transfer effects. This phenomena is important for the combustion process in a layer of fuel particles with a diameter larger than several millimeters. Thirdly, it consists of a limited set of equations, which makes it computationally affordable to use for 2-D studies. The model is here applied with a source term based on coal conversion because this leads to a more simple functional form of the source term than for biomass conversion, while this does not affect the description of the heat loss effects.

This study contains several new results in comparison to previous studies. With respect to the experimental part of this study, there are two new results: (1) The transient front velocity from the start to the end of the experiment is presented and discussed. In most experimental studies, only the transient mass loss and a global velocity is presented (cf. e.g. [16,39,59]), while in other experimental studies only the global velocity is presented (cf. e.g. [57,61]). (2) An experimental estimation of the effect of heat losses is presented by using an insulated and non-insulated reactor. In other experimental studies usually only one reactor configuration is used, or when multiple reactor configurations are used (cf. e.g. [16,57,61]), differences in the results due to the effect of heat losses are not quantified or discussed.

With respect to the numerical part of this study, there are three new results: (1) Spatial reaction front profiles of 1D and 2D configurations for the temperature, oxygen mass fraction and reaction source term based on a situation with heat losses are
presented. In addition, the spatial profile of the heat loss term itself is presented. The effect of heat losses on the front velocity was investigated in Ref. [35] by means of an analytical solution method, but in this study, only spatial flame profiles for the temperature and oxygen concentration are presented valid for a situation with no or asymptotically small heat losses. In Ref. [105] a 2D model for the conversion process in a biomass fuel rod is presented with which heat losses are studied. However, the effect of the instationary heating of the walls of the reactor and preheating of the fuel was not investigated. Furthermore, only the cases of conversion due to a supply of oxygen by free convection and forward combustion (in which the reaction front velocity and the air flow are in the same direction) are investigated. (2) A quantitative comparison between 1D and 2D heat loss effects is performed. Such a comparison is not made by others that account for heat losses [16, 30, 35, 105]. (3) A parametric numerical study of the reactor properties (wall thickness, diameter, conductivity) is performed. Such a parametric study has not been reported by others. The 2D analysis presented in Ref. [105] contains results for one configuration only.

The present chapter focusses on heat losses only. The model therefore contains only a 2D conductivity term, all convective terms are assumed constant. It also means that detailed models that include single particle models and experimental studies with data for the product gas composition are not presented here. These studies can be found elsewhere. The effect of intraparticle gradients is discussed in several modeling studies Refs. [28–30, 52]. These studies also give a detailed representation of the gas phase composition. Other experimental studies that present results for the gas phase composition can for example be found in Refs. [16, 32, 61, 104].

The work presented in this chapter starts with a description of the experimental setup and procedures (Sec. 5.2). This is followed by a presentation of the main experimental results together with an explanation (Sec. 5.2.4). Then, the numerical model, the reactor configurations on which the model is applied and the model results are described (Sec. 5.3). Then, the experimental and numerical results are discussed together (Sec. 5.4). Finally, the conclusions are presented (Sec. 5.5).

5.2 Experiments

This section describes the experimental investigation of the role of heat losses on the front velocity. The experimental plan is presented first (Sec. 5.2.1). This is followed by a description of the setup, a fixed bed reactor equipped with a mass balance and thermocouples (Sec. 5.2.2). Then, the methods used to convert the measurement data into front velocities and mass burning rates is presented (Sec. 5.2.3). Finally, experimental results are discussed obtained with three different reactor configurations (Sec. 5.2.4). These results show the effect of heat losses on the velocity and the spatial profiles of the of the reaction front.

5.2.1 Experimental plan

The goal of the experiments is to investigate the magnitude of the heat loss mechanisms on the velocity of the reaction front. Here, an experimental plan is developed
Table 5.1: Characteristics of reactors used in the literature. A bar in the table indicates that no details about the corresponding reactor characteristic was presented by the author.

<table>
<thead>
<tr>
<th>Principal Author</th>
<th>Shape</th>
<th>r(cm)</th>
<th>h(cm)</th>
<th>Wall Material</th>
<th>Insulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicholls [33]</td>
<td>circle</td>
<td>25.5</td>
<td>112</td>
<td>Refractory lining</td>
<td>-</td>
</tr>
<tr>
<td>Gort [16]</td>
<td>circle</td>
<td>15</td>
<td>80</td>
<td>Thin stainless steel</td>
<td>2 mm ceramic fibre (inside), 100 mm glass wool (outside)</td>
</tr>
<tr>
<td></td>
<td>circle</td>
<td>10</td>
<td>80</td>
<td>Thin stainless steel</td>
<td>2 mm ceramic fibre (inside), 100 mm glass wool (outside)</td>
</tr>
<tr>
<td>Van der Lans [27]</td>
<td>circle</td>
<td>7.5</td>
<td>90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Saastamoinen [57]</td>
<td>circle</td>
<td>11.2</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>square</td>
<td>15</td>
<td>90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Samuelsson [32]</td>
<td>square</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>Well insulated</td>
</tr>
<tr>
<td>Weissinger [31]</td>
<td>circle</td>
<td>6</td>
<td>30</td>
<td>SiC</td>
<td>Loose external casing of firebrick</td>
</tr>
<tr>
<td>Yang [60]</td>
<td>circle</td>
<td>10</td>
<td>150</td>
<td>Inconel liner</td>
<td>Thick layer insulating material in tight casing</td>
</tr>
<tr>
<td>Ryiu [59]</td>
<td>circle</td>
<td>10</td>
<td>150</td>
<td>Inconel liner</td>
<td>8 cm insulation</td>
</tr>
</tbody>
</table>
to achieve this goal. The development of the plan involves the formulation of an hypothesis of 1) how the velocity of the conversion front will vary as a function of the heat loss mechanisms, 2) how the heat losses are affected by reactor design parameters and 3) what reactor designs have to be used in the experiments.

A hypothesis for the impact of the heat loss mechanisms can be formulated on the basis of the simple 1-D analytical expressions for the velocity of the reaction front in a reverse combustion process presented in Ref. [35]. Heat losses to the environment and instationary heating of the reactor walls lead to a decrease of the velocity of the conversion front, as can be derived from the heat loss term in this model. The preheating mechanism leads to a higher velocity of the conversion front. This cannot be derived by an explicit term representing this effect. Instead, it can be deduced by the substituting a higher unburnt fuel temperature resulting from the preheating in the analytical expressions for the front velocity.

The magnitude of the impact of the heat loss mechanisms on the front velocity can be expected to be dependent on the properties of the wall and the insulating layer surrounding it. Increasing the thermal conductivity or reducing the thickness of the insulating layer will increase the effect of heat losses to the environment leading to a reduced front velocity. Increasing the thickness or specific heat of the wall will lead to an increased effect of instationary heating of the reactor walls, which also leads to a reduced front velocity. Increasing the thermal conductivity of the wall will enhance the preheating effect, which results in a higher front velocity.

The reactor designs that are used in the experiments to test the effects of the different heat loss mechanisms make use of (1) different wall materials to vary the magnitude of the wall effects and (2) insulation to vary the effect of heat losses.

To test the effect of insulation, a steel reactor wall with and without insulation was used. By comparing the insulated and uninsulated case, the effect of heat losses to the environment on the front velocity can be observed. Furthermore, because steel is a wall material with a high thermal capacity $\rho_c c_{psw}$ compared to coal and wood fuel layers (cf. Tab. 5.2) it can also be observed if the wall effects become indeed more dominant for an insulated reactor.

To test the effect of wall material, an uninsulated reactor with a quartz wall and a steel wall was used. Quartz has a thermal conductivity close to the thermal conductivity of fuel layers of coal and wood while steel has a thermal conductivity that is much higher than the conductivity of both fuel layers (cf. Tab. 5.2). Another difference is that the thermal capacity $\rho_c c_{psw}$ is much higher for steel than for wood. Thus, a quartz tube, both instationary heating of the reactor walls and heat conduction via the tube walls are potentially less important than for steel.

A reactor design consisting of a quartz wall together with an insulating layer was not used in the experiments. With this configuration a situation with both a low heat loss to the environment and a low effect of the reactor walls could be observed. However, because the quartz wall was sensitive to rupture and mounting the insulating layer on the setup results in extra strain, it was chosen not to use this configuration.

Thus, the experimental plan consists of the measurements with three reactor wall configurations to test the effect of the heat loss mechanisms on the velocity of the conversion front: (1) insulated steel, (2) uninsulated steel, (3) uninsulated quartz.
Table 5.2: Physical properties (density $\rho$, specific heat $c_{ps}$ and conductivity $\lambda$) for quartz and steel. Steel: values for pure iron were used as an approximation. Wood and coal fuel layer properties: added as a reference.

<table>
<thead>
<tr>
<th>material</th>
<th>$T$ (K)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$c_{ps}$ (J g$^{-1}$K$^{-1}$)</th>
<th>$\lambda$ (10$^{-2}$ J K$^{-1}$cm$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>steel [106]</td>
<td>300</td>
<td>7.86</td>
<td>0.425</td>
<td>0.80</td>
</tr>
<tr>
<td>quartz</td>
<td>300</td>
<td>2.20 [107]</td>
<td>0.65 [108]</td>
<td>0.013 [109]</td>
</tr>
<tr>
<td>wood fuel layer$^1$ [16]</td>
<td>973</td>
<td>0.20</td>
<td>2.7</td>
<td>0.01</td>
</tr>
<tr>
<td>coal fuel layer$^1$ [16]</td>
<td>973</td>
<td>0.47</td>
<td>1.8</td>
<td>0.013</td>
</tr>
</tbody>
</table>

$^1$ Values $\rho_s$ and $\lambda$ are effective values for both gas and solid phase. Value for $c_{ps}$ is for the solid phase only.

5.2.2 Setup

The fixed bed reactor (Fig. 5.1) used to study the effect of heat losses on the conversion front consists of a cylindrical tube. The tube is filled with wood particles. Air is supplied at the bottom of the tube with, while the fuel is ignited at the top. After ignition, a reaction front starts to propagate downwards. Measurement equipment (thermocouples and a mass balance) are used to monitor the progress of the conversion process due to the propagating front. (The measurement equipment is not depicted in Fig. 5.1).

The dimensions of the reactor govern the magnitude of the heat loss effects. Relevant dimensions are the inner radius of the reactor $R_i$, the outer radius of the tube wall $R_t$ and the outer radius of the reactor. The wall thickness of the reactor is given by $\Delta R_w = R_t - R_i$, while the thickness of the insulation layer is given by $\Delta R_I = R_o - R_t$. For the quartz tube, $R_i = 31.4$ mm and $\Delta R_w = 2.2$ mm, while for the steel tube, $R_i = 28$ mm and $\Delta R_w = 2.0$ mm. The thickness of the insulation layer applied to the metal tube is given by $\Delta R_w = 4$ cm. The height of the reactor 50 cm.

The measurement data from which the velocity of the conversion front can be calculated is obtained with a series of thermocouples and a mass balance. The thermocouples (K-type and N-type) can be placed in the fuel bed by means of small holes ($d = 0.1$ mm) in the tube wall located at intermediate distances of 5.6 cm. Care is taken to place the tip of the thermocouples at the centerline of the cylinder. The signal of the thermocouples is collected by a TBX-68 thermocouple block of National Instruments, which is connected to a PC. The mass of the entire setup can be monitored with a mass balance (Mettler Toledo BBA425) which is also connected to the PC. Labview software is used to read in the data of both the thermocouples and the mass balance at an interval of about two seconds.

A stable air supply required to create the conditions that allow observations of smaller deviations of adiabatic conversion. The air is supplied at the bottom of the set-up through a circular grid on which the fuel bed rests. The grid contains a distribution of small holes with a diameter of $d = 3$ mm for this purpose. Air is transported to the bottom of the reactor with a plastic hose. The air flow is controlled by a HI-TECH mass flow controller from (INACOM INSTRUMENTS BV) with an
5.2 Experiments

Figure 5.1: Sketch of a fixed bed reactor
The effect of heat losses in reverse combustion experiments

Table 5.3: Proximate and ultimate fuel sample analysis of the spherical hardwood beads and sawdust pellets. All weight percentages on an as received basis. Analysis performed by IVD, Stuttgart University.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta H_r$ (J g$^{-1}$)</th>
<th>$Y_{\text{H}_2\text{O}}$</th>
<th>$Y_{\text{vol}}$</th>
<th>$Y_{\text{ash}}$</th>
<th>$Y_{\text{fc}}$</th>
<th>$Y_{\text{C}}$</th>
<th>$Y_{\text{H}}$</th>
<th>$Y_{\text{N}}$</th>
<th>$Y_{\text{S}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>beads</td>
<td>19889</td>
<td>0.054</td>
<td>0.769</td>
<td>0.011</td>
<td>0.166</td>
<td>0.50</td>
<td>0.61</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>pellets</td>
<td>27135</td>
<td>0.078</td>
<td>0.752</td>
<td>0.050</td>
<td>0.165</td>
<td>0.475</td>
<td>0.058</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
</tbody>
</table>

operating range of 255 nl min$^{-1}$.

The fuel type used in the experiments needs to be quantified because the fuel properties affect (particle size, moisture content, material composition) affect the conversion process. Two types of fuels were used: cylindrical sawdust pellets and spherical hardwood beads. The pelletized sawdust (particle diameter $d_p = 0.6$ cm, varying length) was used because it can be obtained at low costs. This makes it suitable for an elaborate measurement schedule to test an experimental setup as is done in this study. The beads ($d_p = 4$ mm) have the advantage that the experiments are performed under better defined conditions due to their uniform size and shape. Proximate and ultimate analysis of both fuels is presented in table 5.3.

The experimental setup needs to be operated carefully and according to a fixed procedure to obtain reproducible measurements. The procedure starts with setting the mass balance to zero. Then, a fuel sample is brought into the reactor. The amount of fuel used is such that the reactor is filled to 1 to 2 cm below the top of the reactor. The thermocouples are placed in the fuel layer and the air flow is set at the desired level. Data recording in Labview is stated. The the top of the fuel bed is set to fire with firelighters. A conversion front starts to propagate along the reactor wall. The experiment is finished when all the solid fuel in the reactor is converted, which typically takes 1 h to 2 h. An example of raw data obtained during a measurement is presented in Fig. 5.2

5.2.3 Data processing

The ignition rate of the conversion process has to be derived from the experimental data to be able to determine the effect of heat losses. First, we present the definition of the ignition rate. Then, we describe three methods can be followed to do this. Of these methods uses the data from the from the mass balance, while the other two methods make use of thermocouple data.

The ignition rate can be defined as the amount of ignited mass per unit time per unit surface area. It is proportional to the velocity of the conversion front and the apparent density of the solid under unburnt conditions, $\rho_s$:

$$m_{su} = (1 - \epsilon_u) \rho_s v_s,$$

where $\epsilon$ is the bed porosity, $\rho_s$ the density and $v_s$ the conversion front velocity. The subscript $u$ indicates that the porosity should be determined far away from the reac-
5.2 Experiments

Figure 5.2: Raw data from the mass balance (a) and the thermocouples (b). Conditions: \( m_{gu} = 3.3 \times 10^{-2} \) g cm\(^{-2}\) s\(^{-1}\), beads, quartz tube, no insulation.

The ignition rate \( m_{su} \) can be determined from the mass balance data provided that the conversion process occurs in the correct regime. In Ref. [16] three regimes for fixed bed combustion are identified, dependent on the magnitude of the gas mass flow \( m_{gu} \):

1. **Low \( m_{gu} \): Partial gasification**
   The air flow is so low that not all the solid fuel that enters the reaction zone can be oxidized. This results in a growing char layer.

2. **Medium \( m_{su} \): Complete gasification**
   The air flow is sufficiently large to gasify all solid material. A significant mass fraction of CO is present in the reaction zone, while all oxygen is consumed.

3. **Large \( m_{gu} \): Combustion**
   The mass fraction of CO becomes negligible because all carbon is oxidized to CO\(_2\). Oxygen is left in the flue gas.

In the complete gasification regime and the combustion regime, all ignited solid fuel is completely converted into gas. The decrease of \( M \) and the mass burning rate are then directly related by

\[
m_{su} = \frac{1}{A} \frac{dM}{dt}
\]

(5.2)

where \( A \) is the area of the cross-section of the reactor.

The determination of the time derivative in Eq. 5.2 is not straightforward because the output of the weighing balance is a discrete signal. Therefore, it was chosen to perform a local linear fit in the region \([t - \delta t, t + \delta t]\). Here, \( \Delta t = 2\delta t \) is defined as the window size of the fit. During processing of the data, \( \Delta t = 60 \) s, a value large enough to remove the artificial effect of discretization by the mass balance, while at
the same time small enough to observe the instationary behavior of the conversion process.

A second method to determine $m_{su}$ employed in this chapter is based on measurements of the global conversion velocity $v_g$ which can be derived from the thermocouple measurements. The time $t_i$ at which the reaction front passes a thermocouple located at a position $x_i$ is defined as the time at which the thermocouple reaches a temperature of $T_p = 873$ K. The global front velocity can be determined by the time difference of passing of the first and the last thermocouple, i.e.

$$v_{sg} = \frac{x_N - x_1}{t_N - t_1}$$  \hspace{1cm} (5.3)$$

This type of definition is generally used in reverse conversion experiments (cf e.g. [16,32,110]). Due to rapidness of the temperature increase compared to the time it takes for the front to travel the distance between two thermocouples, the velocity obtained by this definition is not very sensitive to the choice of the temperature. Together with the apparent density of the fuel layer $\rho_{sa} = \rho_s (1 - \epsilon_u)$ determined from the initial mass and volume of the fuel layer, $m_{su}$ can be determined on the basis of Eqn. 5.2.

The advantage of using a determination of the global velocity is that it is more accurate, because small uncertainties in the positioning of the thermocouples can be neglected due to the large distance between the thermocouples. Furthermore, it is a valid method for all air flows. A disadvantage of this method is that it offers no insight in the instantaneous front velocity. If the conversion front is not quasi stationary, this may lead to considerable errors in $m_{su}$.

The third method uses the local front velocity $v_{si}$ at the position of thermocouple $i$ to get the local value of the ignition rate, $m_{su,i}$. To determine $v_{si}$, the definition

$$v_{si} = \frac{x_{i+1} - x_i}{t_{i+1} - t_i} \quad i = 1, 2 \ldots N$$  \hspace{1cm} (5.4)$$

is used. Here, $i$ indicates the thermocouple number.

The advantage of the the third method is that it can be used to determine the local velocity of the conversion front during the experiment. Two disadvantages are (1) that positioning errors of the thermocouples can have a large effect on the accuracy on the obtained value of $m_{su}$ due to the small distance between the thermocouples and (2) that the local value of $m_{su}$ obtained with this method is less accurate than the value obtained with the weighing scale.

The front temperature can also be derived from the thermocouples. It can be defined as

$$T_f = \frac{1}{N} \sum_{i=1}^{N} \max (T_i(t)) ,$$  \hspace{1cm} (5.5)$$

i.e. the average of the maximum temperatures measured by the thermocouples.

Summarizing, in this section three methods have been introduced to describe the determination of the front velocity. Each of the methods has its own advantages. In this chapter, all three methods are used. In addition, a definition of the temperature of the reaction front has been presented.
5.2 Experiments

Figure 5.3: The ignition rate as a function of $t$ determined with the mass balance (a) and the thermocouples (b). Conditions: $m_{gu} = 3.3 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$, beads, quartz tube, no insulation.

5.2.4 Experimental results

In order to investigate the effect of heat losses, several experiments were performed and the data was analyzed to determine $m_{su}$ and $T_f$. The experimental investigation starts with measurements of the global ignition rate $m_{sug}$ and $T_f$ as a function of the gas mass flow $m_{gu}$ for an insulated and a non-insulated reactor. Subsequently, the observed differences are investigated further by means of a closer analysis of $m_{su}$ as a function of time for the three reactor configurations.

The measurements of the global ignition rate (cf. Fig. 5.2) consist of measurements with a steel reactor with and without insulation. Both measurements have been performed with wood pellets. The error bars result from the difference in positioning of the thermocouple. With a distance of 50 cm and a positioning error of the first and the last thermocouple of at most 1 cm, the error in the calculation of the front velocity is approximately 4%.

The measurements of the global ignition rate and front temperature without reactor insulation serve as a base case. In these measurements (cf. Fig. 5.2), it can be observed that $m_{su,j}$ increases with increasing gas mass flow, until a maximum is reached. Then, $m_{su,j}$ decreases until extinction takes place at $m_{gu} = 7 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$. The curve for the maximum temperature of the combustion front shows approximately the same behavior. Due to the considerable fluctuations in the observed maximum temperatures (cf. Fig. 5.2) and the fact that the temperatures have not been corrected for radiation, these results are only presented here to describe the trend in the temperature. The line in Fig. 5.4 that represents the ratio of $m_{su}$ and $m_{gu}$ for stoichiometric combustion was determined on the basis of the elemental composition of the fuel, assuming that the products of the combustion process are $\text{H}_2\text{O}$ and $\text{CO}_2$ only. The maximum values of $m_{su}$ and $T_f$ can be found...
close to stoichiometric conditions at \( m_{gu} \sim 3 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1} \).

The effect of insulation on \( m_{su} \) and \( T_f \) was investigated is also presented in Fig. 5.2. At low values of \( m_{gu} \), i.e. \( m_{gu} \lesssim 3 \times 10^{-3} \text{ g cm}^{-2} \text{s}^{-1} \), the effect of insulation is not significant. At higher values, i.e. for \( m_{gu} \sim 3 \times 10^{-3} - 7 \times 10^{-3} \text{ g cm}^{-2} \text{s}^{-1} \), the ignition rate \( m_{su} \) becomes higher than in the uninsulated case. For \( m_{gu} = 6 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1} \), the difference becomes more than 30%. The front temperature seems to increase also when insulation is applied for higher values of \( m_{gu} \), but here only one measurement point (i.e at \( m_{gu} = 6 \times 10^{-2} \)) can be used to support this statement. For the other measurement points, this effect is not significant.

The effect of insulation and wall material was investigated further in experiments from which the instantaneous value of \( m_{gu} \) was determined. For these experiments, the hardwood particles were used. Raw data from the mass balance and thermocouples is presented in Fig. 5.4a. The bed mass \( M(t) \) is not scaled with \( M(0) \), because this would change the slope of the curve, which represents the conversion rate. From the data for \( M(t) \), it can be observed that the decrease of the mass is almost linear for a quartz reactor wall. In case of a steel reactor wall, the curve for the mass loss starts to deviate from a straight line. For an insulated steel reactor, this deviation starts to become stronger. Data from the thermocouples (cf. Fig. 5.4b) is presented for an insulated and uninsulated reactor only. It can be seen that in case of an insulated reactor, the temperature decrease is low when the reaction front has just passed the thermocouple. For the uninsulated reactor this temperature decrease is much more rapid. For \( T_f \), it is difficult to draw conclusions, because this quantity fluctuates rapidly (cf. Fig. 5.2).

The raw data of the measurements with different reactor wall material and insulation have been processed according to the methods described in Sec. 5.2.3. The results (cf. Fig. 5.6) show that this quantity is almost constant after a short ig-
5.2 Experiments

Figure 5.5: The effect of wall material and insulation on the bed mass $M(t)$ (a) and the thermocouple temperature $T$ (b) for a quartz (dashed-dotted), steel (dashed) and insulated steel reactor wall (solid line). The temperature $T(t)$ for a quartz tube is not presented. Conditions: $m_{su} = 3.3 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1}$, beads.

nition phase for measurements with the quartz reactor wall. With the iron reactor walls, the front velocity does not become constant. It increases from $m_{su} \sim 0.4 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1}$ at $t \sim 0$ min to $m_{su} \sim 0.7 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1}$ at the end of the experiment. Initially, it is lower than the value for a quartz wall, but around $t \sim 32 \text{ g cm}^{-2} \text{s}^{-1}$, $m_{su}$ becomes higher than this value. If insulation is applied, the observed effects with a steel reactor wall become stronger. The observed value of $m_{su}$ is higher than for the uninsulated steel wall during the entire experiment. Furthermore, the effect of an increasing front velocity becomes stronger. It increases from $m_{su} \sim 0.7 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1}$ at $t = 20$ min to $m_{su} = 0.6 \times 10^{-2} - 0.8 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1}$ at the end of the experiment. The final value of $m_{su}$ observed during the experiment ($m_{su} = 0.8 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1}$) is highest values observed during all experiments.

The measurements of the ignition rate can be explained by the properties of the reactor wall. The quartz tube wall has a low specific heat and conductivity. The low specific heat and conductivity initially result in a value of $m_{su}$ that is close to the final value of the experiment, because it means that the heating of the tube walls during the formation of a stationary reaction front structure plays only a small role. In a later stage, this causes the propagation of the reaction front to be almost constant, because the effect of transport of heat from the reaction zone via conduction by the walls is small. Because of the larger specific heat and conductivity of the steel wall, the velocity of the reaction front is initially lower, while it keeps increasing due to the stronger heat transport via the tube walls. Finally, the insulated steel tube gives rise in a higher ignition rate during the start of the experiment in comparison with the uninsulated case because heat losses to the environment are less important. The higher increase of the ignition rate during the rest of the experiment can also be explained by the reduced heat loss to the environment. Because less heat is lost to the environment, more heat will be transported via the tube walls to the unburnt fuel. The reduced heat losses to the environment and the preheating effect together
result in the highest front velocity observed at $m_{gu} = 0.3 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$ for the various.

The ignition rates $m_{sui}$ determined with the thermocouples (cf. Fig. 5.4) confirm the results already observed in the instantaneous velocity of the reaction front for the variation in reactor design. However, for all measurements, the first point where $m_{sui}$ is determined results in a value that considerably exceeds the value derived from the mass loss data. The cause for this was not found in the present study. In addition, the values for $m_{sui}$ show a large uncertainty which is an inherent problem of using this method (cf. Sec. 5.2.3).

The experimental results described in this section show that the properties of the reactor have a significant effect on the conversion process. The global velocities are significantly affected by the presence of an insulating layer around the setup. The curves for the instantaneous values of the ignition rate for an insulated and uninsulated reactor confirm this result. The measurement with the quartz reactor wall shows that a material with a low conductivity and specific heat results in a constant front velocity because the effects of heat transport via the reactor walls and instationary wall heating are only small. In contrast, these effects are large in case of an insulated reactor with a steel wall.

### 5.3 Simulations

In this section 1-D and 2-D simulations are described. The effect of heat losses on the conversion process has been illustrated experimentally in Sec. 5.2. In this sec-
tion, simulations are described to investigate how to deal with these effects in when validating of 1-D numerical models. Two approaches are followed: (1) take the heat losses into account with an effective heat loss term in the 1-D model and (2) use 2-D simulations of a reactor with heat losses for the design of an experimental reactor in which the effect of heat losses is minimized. For the first approach, a comparison between numerical simulations with a 1-D and 2-D model is made. For the second approach, a parameter study in which several parameters \( R_t, \Delta R_w, \lambda_w \), are varied.

The further outline of this section is as follows. First, the 2-D model is presented (Sec. 5.3.1) followed by a description of the 1-D model, which is a special case of the 2-D model. Subsequently, the data used in for both models is presented (Sec. 5.3.3). Finally, the results obtained in the numerical investigation are described (5.3.4). Then, the results obtained for the different cases are presented (Secs. 5.3.5-5.3.8).

### 5.3.1 2-D model equations

The configuration that is described with the 2-D model consists of four domains: (1) the fuel layer, (2) the reactor walls and (3) the environment. The fuel layer and the reactor walls are modeled with transport equations. For the transport equations for the fuel layer, a 2-D description of the model presented in Refs. [1,16,34] is used. For the transport equation for the tube wall, a temperature equation is used. For the free convection occurring in the environment of the reactor, a heat transfer coefficient is used in the boundary condition at \( R_t \) for the temperature equation. This means that for the environment, no transport equations are solved.

#### Fuel layer

The model equations for the fuel layer are written in terms of cylindrical coordinates corresponding with the coordinate system in Fig. 5.1. Because of radial symmetry, a tangential coordinate \( \theta \) is not used here. The model equations consist of equations for the porosity of the fuel layer, the oxygen mass fraction and the temperature. The solid fuel porosity \( \epsilon \) is given by

\[
\frac{\partial}{\partial t} \left( (1 - \epsilon) \rho_s \right) = -R. \tag{5.6}
\]

Here, \( t \) is the time, \( \epsilon \) is the porosity of the solid, \( \rho_s \) the solid density and \( R \) the reaction source term. The second equation is the equation for the mass fraction of oxygen \( Y \), given by

\[
\frac{\partial}{\partial t} \left( \epsilon \rho_g Y \right) + \nabla \cdot \left( \epsilon \rho_g v_g Y \right) - \nabla \cdot \left( \rho_g D \nabla Y \right) = -\omega R. \tag{5.7}
\]

Here, \( \rho_g \) is the gas density, \( v_g \) the gas velocity, \( D \) a dispersion coefficient and \( \omega \) a mass based stoichiometric coefficient. The equation for the gas-solid equilibrium temperature is represented by

\[
\frac{\partial}{\partial t} \left( (\epsilon \rho_g c_{pg} + (1 - \epsilon) \rho_s c_{ps}) T \right) + \nabla \cdot \left( \epsilon \rho_g v_g c_{pg} T \right) - \nabla \cdot \left( \Lambda \nabla T \right) = -\Delta H_r R. \tag{5.8}
\]
Here, \( \rho \) is the density, \( R \) the reaction source term, \( v_g \) the gas velocity, \( \Lambda \) the conductivity coefficient and \( \Delta H_r \) the reaction enthalpy.

In this study, additional assumptions are made in the set of Eqs. 5.6-5.8. The gas velocity is assumed to have only an axial component in the \( z \)-direction, i.e.

\[
v_g = v_g e_z,
\]

where \( e_z \) is the basis vector in the \( z \)-direction. In addition, the tensors \( \Lambda \) and \( D \) are assumed to be isotropic, which means that they can be replaced by the scalars \( \Lambda \) and \( D \). This means that the set of Eqs. 5.6-5.8 can be written as

\[
\frac{\partial}{\partial t} (\rho v_g Y) + \frac{\partial}{\partial z} (\rho v_g v_g Y - (1 - \epsilon) \rho_s c_{ps} T) - \frac{\partial}{\partial r} (r \Lambda \frac{\partial T}{\partial r}) - \frac{\partial}{\partial z} (\rho_g D \frac{\partial Y}{\partial z}) = -R
\]

(5.10)

\[
\frac{\partial}{\partial t} (\epsilon \rho g c_{pg} + (1 - \epsilon) \rho_s c_{ps} T) + \frac{\partial}{\partial z} (\epsilon \rho g v_g v_g T) - \frac{1}{r} \frac{\partial}{\partial r} (r \Lambda \frac{\partial T}{\partial r}) - \frac{\partial}{\partial z} (\Lambda \frac{\partial T}{\partial z}) = -\Delta H R
\]

(5.11)

The gas mass flow is assumed constant, i.e.

\[
m_g = m_{gu},
\]

(5.13)

which means that a continuity equation is not solved. This is also done in Refs. [1, 16, 34]. In Ref. [1] it is shown that applying this assumption does not lead to a difference in the general dependence of \( m_{su} \) on \( m_{gu} \). Boundary conditions at the unburnt and the burnt side of the fuel layer are given by

\[
Y|_u = Y_u, \quad T|_u = T_u, \quad \frac{\partial Y}{\partial z}|_b = 0, \quad \frac{\partial T}{\partial z}|_b = 0.
\]

(5.14)

The boundary conditions at the inner wall are given by

\[
\frac{\partial Y}{\partial r}|_{r=r_i^-} = 0, \quad \Lambda \frac{\partial T}{\partial r}|_{r=r_i^-} = \lambda_w \frac{\partial T}{\partial x}|_{r=r_i^+}.
\]

(5.15)

Equations 5.6-5.8 together with the boundary conditions in Eqs. 5.14 and 5.15 give a complete description of the fuel layer.

**Reactor wall**

The temperature equation for the reactor wall is given by

\[
\rho_w \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_w \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \lambda_w \frac{\partial T}{\partial z} \right)
\]

(5.16)
Boundary conditions at the unburnt and burnt side are given by

\[ T|_u = T_u, \quad \frac{\partial T}{\partial z}|_b = 0. \]  

(5.17)

The boundary equation at the inner surface of the reactor wall is given by Eq. 5.15.

The boundary condition at the outer wall is given by

\[ -\lambda_i \frac{\partial T}{\partial r}|_{r=r_o} = k_h (T - T_u) \]  

(5.18)

where \( k_h \) is a heat transfer coefficient representing free convection and \( T_u \) is the unburnt temperature, which is assumed to be equal to the temperature of the surroundings.

### 5.3.2 1-D model equations

The 1-D set is similar to the 2-D set of model equations, Eqs. 5.6-5.8, except for the representation of heat losses. It is given by:

\[ \frac{\partial}{\partial t} ((1 - \epsilon) \rho_s) = -R \]  

(5.19)

\[ \frac{\partial}{\partial t} (\epsilon \rho_g Y) + \frac{\partial}{\partial z} (\epsilon \rho_g v_g Y) - \frac{\partial}{\partial z} \left( \rho_g D \frac{\partial Y}{\partial x} \right) = -\omega R \]  

(5.20)

\[ \frac{\partial}{\partial t} \left( (\epsilon (\rho_g c_{pg} + (1 - \epsilon) \rho_s c_{ps}) T) + \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial}{\partial z} \left( \Lambda \frac{\partial T}{\partial x} \right) \right) \right) = -\dot{q}_p - \dot{q}_l \]  

(5.21)

with boundary conditions given by 5.17. Here, the source terms in the temperature equation are a production term due to the chemical reaction,

\[ \dot{q}_p = -\Delta H_r \]  

(5.22)

and a loss term due to the heat losses to the environment.

\[ \dot{q}_l = k_h \frac{P}{A} (T - T_b) \]  

(5.23)

is used, where \( P \) is the perimeter of a radial cross-section of the tube. In the 1-D configuration, the reaction wall is not modeled and therefore \( R_0 \) is the outer radius of the tube. For a circular cross-section,

\[ \frac{P}{A} = \frac{2}{r}, \]  

(5.24)

which means that \( \dot{q}_l \) is inversely proportional to the tube radius.

It can be observed that in comparison with Eqs. (5.6)-(5.8) the radial dispersion of mass and heat is no longer represented in Eqs. (5.20) and (5.21). Furthermore, in the equation for the temperature (Eq. 5.21), the sink term \( \dot{q}_l \) is introduced to account for heat losses to the environment. In a 1-D approach, these heat losses can no longer be represented in the boundary conditions, hence they are modeled as a sink term in the temperature equation.

The set of equations given by Eqs. 5.19-5.21 with boundary conditions given by 5.17 gives a complete description of a 1-D conversion process taking into account heat losses to the environment.
5.3.3 Model data and additional expressions

To perform calculations with the model equations in Secs. 5.3.2, 5.3.1 additional expressions and data is required. The model is used with a data set for coal conversion.

Expressions for the reaction source term \( R \), the dispersion coefficient \( D \), the conductivity coefficient \( \Lambda \) and the heat transfer coefficient \( k_h \) are required to solve the model. To obtain an expression for the source term \( R \), the heterogeneous surface reaction of coal with oxygen

\[
C + \omega O_2 \rightarrow (1 + \omega) CO_2,
\]

is used. As measurements using coal fuel layers indicate that the primary product in the reaction zone is \( CO_2 \) [16], this is a reasonable approach. Modeling the conversion of solid fuels by a single step reaction is commonly applied in the literature, for example in the reverse smolder models [36, 38, 88, 89] and for the devolatalization step in many biomass conversion models [26, 30, 52].

For the source term, a shrinking core model is applied. This implies that the coal particles (in contrast to the fixed bed) are modeled as a non-porous medium. Thus, the conversion process occurring in a thin layer below the particle surface is not explicitly represented. However, this process is assumed to be represented implicitly in the source term by the use of effective kinetic parameters, which in turn makes \( R \) an effective source term.

Applying a shrinking core model for \( R \), leads to the expression [16]

\[
R = \frac{1}{k_r^{-1} + k_m^{-1} S_u \left( \frac{1 - \epsilon}{1 - \epsilon_u} \right)^{2/3}} \rho_y Y. \tag{5.26}
\]

Here, \( k_r \) is the reaction rate constant, \( k_m \) a mass transfer coefficient and \( S_u \) the internal surface area per unit volume of the fuel bed for unburnt conditions. The instantaneous internal surface area is represented by \( S_u \left( \frac{1 - \epsilon}{1 - \epsilon_u} \right)^{2/3} \) in this expression. For spherical particles of diameter \( d_p \) in an SC (simple cubic) structure, the \( S_u \) is given by

\[
S_u = \frac{\pi}{d_p}. \tag{5.27}
\]

For \( k_r \) an Arrhenius rate is used:

\[
k_r = A_f T \exp \left( - \frac{E_a}{R_y T} \right). \tag{5.28}
\]

Expressions for the gas density, the effective conductivity, the dispersion coefficient and the mass transfer coefficient are needed. The gas density is given by the ideal gas law at constant pressure

\[
\rho_y = \rho_{gu} \frac{T_u}{T}. \tag{5.29}
\]

The effective dispersion coefficient for heat conduction is given by Ref. [16]

\[
\Lambda = \lambda_{s0} + 0.8 m_{gu} c_pg d_p. \tag{5.30}
\]
where \( \lambda_{o0} \) is the conductivity of the stagnant bed. The second term is the conductivity due to the contribution of the flow. The dispersion coefficient is given by [16]

\[
D = \frac{v g u d_p}{2}.
\]

To calculate the mass transfer coefficient \( k_m \), the correlation for the particle Sherwood number,

\[
Sh_p = 2 + 0.81 \epsilon^{-1/2} Re_p^{1/2} Sc^{1/4} \quad 0 < Re_p < 500
\]

(5.32)
can be used [91]. Here, the particle Sherwood number \( Sh_p \) (the dimensionless mass transfer coefficient), particle Reynolds number \( Re_p \) and Schmidt number \( Sc \) are given by:

\[
Sh_p = \frac{k_m d_p}{D}, \quad Re_p = \frac{U d_p}{\nu}, \quad Sc = \frac{\nu}{D}.
\]

(5.33)

Here, \( \nu \) is the kinematic viscosity of the gas in the fuel layer. The diffusion coefficient \( D \) and the viscosity \( \nu \) are obtained from correlations presented in Ref. [97].

The effect of heat losses to the environment is described with a heat transfer coefficient \( k_h \). This coefficient is obtained from a correlation presented in Ref. [111] for free convection around a vertical tube to estimate the magnitude of the transfer to the environment:

\[
Nu_t = 0.6 \left( Ra_t \frac{d^3}{L} \right)^{0.25}.
\]

(5.34)

where the Nusselt number \( Nu_t \), i.e. the dimensionless heat transfer coefficient, and the Raleigh number, i.e. the dimensionless ratio of convective and conductive transport, are given by

\[
Nu_t = \frac{k_h d_t}{\lambda_o}, \quad Ra_t = \frac{g \beta_o (T_R - T_u) d^3}{\nu_o \lambda_o}.
\]

(5.35)

In these relations, \( \lambda_0 \) is the conductivity of the air, \( g \) is the gravitational acceleration, \( \beta \) the thermal expansion coefficient, \( T_R \) the temperature evaluated at \( r = R_i \) (case without tube wall) or \( r = R_t \) (case with tube wall). For the thermal expansion coefficient, the approximation for an ideal gas given by

\[
\beta = \frac{1}{T_u}
\]

(5.36)
is used. For the quantities \( \lambda_0 \) and \( \nu_0 \) correlations from Ref. [97] were used, substituting the film temperature \( T_f = \frac{T_u + T_i}{2} \).

For the description of the material parameters of the solid fuel layer and the gas flow, a list of parameters is presented in Tab. 5.4. For the material properties of the metal reactor walls, data supplied from a database from the software package ‘Comsol’ [112] was used. This means that \( \rho_w = 7.87 \text{ g cm}^{-3}, c_{pw} = 0.44 \text{ J g}^{-1} \text{K}^{-1}, \) and \( \lambda_w = 0.762 \text{ J cm}^{-1} \text{s}^{-1} \text{K}^{-1} \).

The additional expressions presented here together with the transient and stationary formulation of the model equations are implemented in the commercial
The effect of heat losses in reverse combustion experiments

Table 5.4: Physical parameters used for the calculations for a propagating reaction front in a bed of coal particles [16].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_u$</td>
<td>K</td>
<td>288</td>
</tr>
<tr>
<td>$\Delta H_r$</td>
<td>J g$^{-1}$</td>
<td>$-28.9 \times 10^3$</td>
</tr>
<tr>
<td>$c_{ps}$</td>
<td>J g$^{-1}$K$^{-1}$</td>
<td>1.8</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>g cm$^{-3}$</td>
<td>$1220 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\rho_{sa}$</td>
<td>g cm$^{-3}$</td>
<td>$470 \times 10^{-3}$</td>
</tr>
<tr>
<td>$d_p$</td>
<td>cm</td>
<td>2.5</td>
</tr>
<tr>
<td>$\lambda_s$</td>
<td>J cm$^{-1}$s$^{-1}$K$^{-1}$</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\rho_{gu}(T_u)$</td>
<td>g cm$^{-3}$</td>
<td>$1.226 \times 10^{-3}$</td>
</tr>
<tr>
<td>$c_{pg}$</td>
<td>J g$^{-1}$K$^{-1}$</td>
<td>1.13</td>
</tr>
<tr>
<td>$Y_u$</td>
<td>-</td>
<td>0.23</td>
</tr>
<tr>
<td>$A_f$</td>
<td>cm K$^{-1}$s$^{-1}$</td>
<td>$6 \times 10^4$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>kJ mol$^{-1}$</td>
<td>150</td>
</tr>
<tr>
<td>$\omega$</td>
<td>-</td>
<td>2.67</td>
</tr>
</tbody>
</table>

package ‘Comsol’. This package was chosen because has two advantages: (1) it provides an appropriate platform to perform simulations in a multidimensional coordinate system and (2) it can deal adequately with configurations that contain different materials and regions with interfaces in between them. Both advantages are exploited here.

5.3.4 Cases

In order to investigate the effect of heat losses, numerical simulations with six configurations are used. These configurations can be found in Tab. 5.5.

Case 1 and 2 consist of 1-D simulations with and without heat losses. These simulations are used to obtain more insight in the general effect of heat losses on the flame structure. Only heat loss effects to the environment is considered in case 2.

Case 3 consist of a 2-D simulation with heat losses to the environment without wall effects. It is used to compare the 1-D representation of these losses by means of a volumetric heat loss term to a full description of heat losses to the environment with in the 2-D simulations. This case can be obtained by letting $\Delta R_w \rightarrow 0$ in the 2-D model equations. An investigation of how well the other heat loss mechanisms (instationary heating of the reactor walls and preheating of the unburnt fuel) can be represented in the 1-D model is not investigated in this chapter.

Case 4 and 5 consists of simulations with steel reactor walls. In case 4, a perfectly insulated reactor is used. In case 5, a situation without insulation, but with free convection around the reactor is described. A practical situation will be in between these limits. Therefore, case 4 and 5 can be used to estimate the maximum and the minimum effect of heat losses.

The configurations of the different cases are used in this chapter for a parametric
Table 5.5: Cases used in the numerical simulations. Wall effects stands for both instationary heating of the reactor walls and preheating of the unburnt fuel.

<table>
<thead>
<tr>
<th>Case</th>
<th>Dimension</th>
<th>Heat loss mechanism</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-D</td>
<td>adiabatic conversion</td>
<td>$k_h \rightarrow 0$</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>free convection</td>
<td>$k_h \neq 0$</td>
</tr>
<tr>
<td>3</td>
<td>2-D</td>
<td>free convection</td>
<td>$k_h \neq 0, \Delta R_w \rightarrow 0$</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>wall effects</td>
<td>$k_h \rightarrow 0, \Delta R_w \neq 0$</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>wall effects and free convection</td>
<td>$k_h \neq 0, \Delta R_w \neq 0$</td>
</tr>
</tbody>
</table>

Table 5.6: Default values for the numerical simulations

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_i$</td>
<td>(cm)</td>
<td>10</td>
</tr>
<tr>
<td>$\Delta R_w$</td>
<td>(cm)</td>
<td>0.2</td>
</tr>
<tr>
<td>$m_{gu}$</td>
<td>(g cm$^{-2}$ s$^{-1}$)</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

study to investigate the effect of reactor design parameters on the front velocity. For this parameter study, all parameters are kept fixed except the parameter that is investigated. The fixed set of parameters is given in Tab. 5.6.

5.3.5 1-D simulations: general effect of heat losses

The 1-D set of equations was used first to determine the effect of heat losses on the spatial profile of the temperature of the conversion front and on the main parameters of the combustion process, i.e. the ignition rate $m_{su}$, the front temperature $T_f$ and the conversion $\epsilon_b$. Case 1 and Case 2 were used for this.

The spatial profile of the temperature for the set of 1-D model equations including $\dot{q}_l$ is presented in figure 5.7a together with the evolution $T_f$ and $m_{su}$ (case 2). The simulation was started at $t = 0$ min by using the result of an adiabatic simulation (case 1). The adiabatic nature of the initial profile can be seen from the constant value of $T$ at the bunt side of the domain. During the conversion process, the profile changes in two aspects: (1) the maximum temperature $T_f$ changes and (2) the temperature behind the conversion front decreases. Both changes result in the formation of a new stationary solution. It can be seen that $T_f$ and $m_{su}$ reach their final, stationary value very rapidly (at $t \sim 100$ min), while the change in the spatial temperature towards values close to $T_u$ takes much longer.

The effect of the magnitude of the heat losses to the environment on the front parameters is presented in Fig. 5.8. For these simulations, the value for $k_h$ was varied by taking the maximum value in the results, i.e. $k_{h0} = \max (k_h)$ for ($m_{gu} = 0.25 \times 10^{-2}$ g cm$^{-2}$ s$^{-1}$) and assuming a constant value for $k_h/k_{h0}$ in the simulations. Results are described in Fig. 5.7. The volumetric heat production by the reaction source term $\dot{q}_p$ and the volumetric heat loss term $\dot{q}_l$ (Fig. 5.7a) show that an increasing value of $k_h$ results in a decrease of $\max (\dot{q}_p)$ and $\max (\dot{q}_l)$. The location of $\max (\dot{q}_p)$
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Figure 5.7: The effect of a 1D heat loss term on spatial profiles of $T(x)$ (a) and on $m_{su}(t)$ and $T_f(t)$ (b) (case 2). Profiles $T(x)$ for $t = (0:20:300)$ min. Initial profile ($t = 0$ min): adiabatic solution (case 1).

is also shifting towards $\max(q_r)$.

The results for the other parameters $m_{su}$, $T_f$ and $\epsilon_b$ (cf. Figs. 5.8a,b and c) show that the effect of heat losses is a strong decrease of $m_{su}$ from $m_{su} = 0.2 \times 10^{-2}$ to $m_{su} = 0.05 \times 10^{-2}$ when $k_h/k_h0$ is increased from 0 to 1.75. At the same time, the conversion increases significantly from $\epsilon_b = 0.65$ to $\epsilon_b = 0.75$. The temperature $T_f$ decreases only slightly from $T_f = 1250$ K to $T_f = 1170$ K.

The results of the spatial profiles and the model equations show that heat losses affect $m_{su}$ and $T_f$ only insofar they affect the reaction zone of the flame. This becomes clear from the transient temperature profiles and the values of $m_{su}$ and $T_f$ presented in Fig. 5.7: as soon as the shape of the temperature curve near the reaction zone (i.e. close to the maximum temperature) becomes constant, the main flame parameters $m_{su}$ and $T_f$ becomes constant.

In the classical study of reverse combustion by Lozinski and Buckmaster [35] the effect of small volumetric heat losses on $T_f$ and $m_{su}$ was investigated by analytical methods. Their results are in agreement with the results presented in this paper. Their observations were that $m_{su}$ decreases significantly with increasing heat losses, while $T_f$ stays approximately constant. (In terms of their analysis method based on asymptotic series using the dimensionless inverse activation energy, the deviations due to first order heat losses lead to first order deviations in $m_{su}$ and second order deviations in $T_f$). However, the results presented here include spatial flame profiles, which offer additional insight in the effect of heat losses. Furthermore, the set of equations and the source term that are used here are more general, because an additional equation for the porosity is solved and the effect of mass transfer limitations is accounted for in the reaction source term. That the observations in Ref. [35] also hold for the source term used in the present case is not straightforward, as such
5.3 Simulations

A source term may lead to a different spatial front structure (cf. [1]), thus leading also to a different dependence on heat losses.

The increasing heat losses cause an increased conversion $\epsilon_b$ and a decrease of the conversion front velocity. As illustrated by the results in this paper and supported by the analysis in Ref. [35] the temperature of the reaction zone remains almost constant, while increasing the heat losses. This means that the heat release by the conversion process $\dot{q}_r$ increases. The mechanism by which this occurs is a reduced velocity of the conversion front (or equivalently, a reduced value of $m_{su}$). From the results in this paper, it can be concluded that this means that the conversion front consumes a larger part of the solid fuel, hence the increased value of $\epsilon_b$.

The consequence of the 1-D results presented here is that they indicate that for accurate measurements of $m_{su}$ and $T_f$ in the presence of heat losses, the length scale of the quasi-stationary spatial profile is not important for the reactor design. Instead, the height of the reactor $L$ and the typical spatial extent of the reaction zone $\delta_R$ should follow the relationship $R \gg \delta_R$.

5.3.6 1-D versus 2-D simulations: free convection

Here, 2-D model results are presented and compared to the 1-D results (case 2 versus case 3) to investigate the quality of the representation of free convection in the 1-D model. Firstly, transient results for $m_{su}$ are presented and compared to the 1-D results. Secondly, 2-D model results illustrating the dependency of $m_{su}$ on the reactor diameter are shown. Thirdly, spatial profiles of $T$ and $q_p$ are presented to provide more insight in the transient behavior of $m_{su}$.

The results of 2-D simulations show that $m_{su}$ decreases due to the effect of heat loss to the environment, similar to the results of the 1-D simulations. However, three important differences can be observed: (1) shortly after starting the simulation, $m_{su}$ remains close to the adiabatic value, (2) the decrease of $m_{su}$ is more rapid in the 1-D results and (3) the stationary value of $m_{su}$ is closer to the adiabatic result for the 2-D simulations than for the 1-D simulations. The difference between the 1-D results and 2-D results is in the order of 10%. Observed differences (1) and (2) are related to the transient behavior of the conversion process, while (3) is related to the quasi-stationary propagation phase.

The differences in the transient behavior of $m_{su}$ can be explained by the time needed for the transport of heat in the axial direction in the 2-D simulations. The starting solution was obtained under adiabatic conditions. The effect of heat losses influences the conversion process near the tube walls first. The heat transport of regions closer to $r = 0$ cm the center line is starting up more gradual, which means that the central region of the reactor notices the effect of heat losses last. During this process, a new stationary structure of the front is formed, resulting in a constant value of $m_{su}$. Because the velocity of the conversion front is determined at $r = 0$ and this region initially is not affected by heat losses, the local velocity of the conversion front is close to the adiabatic velocity. In case of the 1-D results, there is no distinction of regions in the radial direction and the effect of the volumetric heat loss term influences $m_{su}$ instantaneously.
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Figure 5.8: The effect of a 1D heat loss term on the profiles of $q_r$, $q_l$ and the values of $m_{su}$, $T_f$ and $\epsilon$ (case 2). Conditions: $k = k_h = k_{h0} = 9.5 \times 10^{-4}$. Curves for $q_r$ and $q_l$: $k_h = k_{h0}$ (solid line), $k_h = 1.25k_{h0}$ (dashed line), $k_h = 1.5k_{h0}$ (dashed-dotted line) and $k_h = 1.75k_{h0}$ (solid line). Alignment of $q_r$ and $q_l$ curves: $\max(\dot{q}_r)$ is located at $z = 0$. 
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Figure 5.9: The effect of heat losses on $m_{su}$ in predictions of the 2D-model (solid line, case 3). Reference results: simulations under adiabatic conditions (dotted line) and 1D simulations with a volumetric heat loss term (dashed line, case 2).

The difference in the value of $m_{su}$ can be attributed to the value of $T$ used in the determination of the magnitude of the heat losses. In case of 2-D simulations, the value $T(r = R_0, z)$, i.e. the temperature of the surface of the fuel layer, is substituted in the boundary condition that represents the heat loss (Eqn. 5.18). In case of 1-D simulations, only the temperature $T(z)$ is available. Consequently, it is used in the expression for $\dot{q}$. Because $T(r = R_0, z) \leq T(r = 0, z)$, the 1-D approach overestimates the effect of heat losses, leading to a overestimation of the decrease of $m_{su}$ due to heat losses.

In order to investigate the difference in the value of $m_{su}$ during the quasi-stationary propagation phase further, simulations with different reactor radii were used. In Fig. 5.10 spatial profiles of $T$ and $q_p$ are shown for $R_i = 10$ cm and $R_i = 10$ cm. In the axial direction, the spatial profiles of $T$ are similar as the 1-D profiles presented in 5.7. At the upstream side of the reaction zone the fuel is preheated. Close to the maximum temperature, the reaction zone is located. Behind the reaction zone, the temperature decreases. In the radial direction, the profiles show gradients due to the heat transport to the reactor surroundings. The temperature near the walls is lower than the temperature in the center of the reactor. The heat losses result in a curved reaction zone, because due to the effect of heat losses, the progression of the front lags behind in the regions close to the tube wall.

The main difference between temperature profiles for different radii presented in Fig. 5.10 can be observed in the high temperature region indicated with the bold isotherm ($T > 1200$ K). In the case $R_i = 20$ cm, this region extends over a range $\Delta z > 15$ cm for $r = 0$, while for the case $R_i = 10$ cm, this value is $\Delta z \sim 5$ cm. This means that the effect of heat losses becomes stronger in the reaction zone for smaller reactor diameters. This is the same effect as described in Fig. 5.7, where it was observed for a change in $k_h$ in a 1-D situation.

The effect of the reactor radius on the conversion velocity is presented in Fig. 5.11. It can be observed that the effect of heat losses decreases strongly with increasing $R_i$; for $R_i = 5$ cm, an ignition rate of $m_{su} = 0.125$ g cm$^{-2}$s$^{-1}$ is observed, while
Figure 5.10: The effect of heat losses to the environment on $T$ (a,b) and $\dot{q}_p$ (c,d) for a configuration without rube walls (case 3). Left: $R_i = 10$ cm. Right: $R_i = 20$ cm. Isolines at $T = (300 : 100 : 1200)$ K, $\dot{q}_p = (1 : 1 : 3) \text{ J cm}^{-3}\text{s}^{-1}$. The highest isolines are printed bold.
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Figure 5.11: The effect of $R_i$ on $m_{su}$ without tube walls (case 3). Reference results: 1-D adiabatic simulations (dotted line, case 1).

for $R_i = 30$ cm a velocity of $g \text{ cm}^{-2} \text{s}^{-1} = 0.19 \text{ g cm}^{-2} \text{s}^{-1}$ is obtained. This is an increase of around 50%. Furthermore, it can be seen that for a reactor diameter of $R_i = 30$ cm the difference with the adiabatic value of $m_{su}$ is around 5%. Because $m_{su}$ approaches its adiabatic value very slowly when $R_i$ is increased further, increasing $R_i$ to increase the measurement accuracy is not an option.

The comparison between the two approaches to describe heat losses, i.e. using a 1-D model with an effective heat loss term and using a 2-D model to resolve the radial heat transport, shows that the differences between the results is significant. These differences affect the transient behavior of the conversion process as well as the quasi-stationary behavior. Because the 1-D simulations overestimate the heat losses, 2-D simulations should be used.

5.3.7 2-D simulations: wall effects

The results in this section describe the effect of the reactor walls on the conversion process for an adiabatic reactor. The results consist of transient calculations of $m_{su}$ for different reactor radii, spatial profiles of $T$ and $\dot{q}_p$ and results for $m_{su}$ as a function of the reactor design parameters $\Delta R_w$ and $R_i$. Furthermore, the effect of the conductivity of the reactor walls is illustrated.

The transient results for $m_{su}$ are presented in Fig. 5.12. It can be observed that the presence of tube walls initially results in a high value of $m_{su} = 0.3 \times 10^{-2}$ g cm$^{-2}$s$^{-1}$ which decreases when the solution becomes quasi-stationary. Then, values of $m_{su} \sim 0.225 \times 10^{-2}$ are observed, which is around 10% higher than the adiabatic value of $m_{su}$ without the effect of reactor walls. The value of $m_{su}$ for $R_o = 10$ cm is slightly higher than for $R_o = 20$ cm, indicating that the effect of the reactor walls becomes increasingly important with decreasing reactor radius. Furthermore, it can be observed that there is a considerable effect of the boundary condition $T(z = L) = T_u$ due to the high conductivity of the metal walls.

In the spatial temperature profiles of the simulations (cf. Fig. 5.13) the effect of the presence of reactor walls can be observed. It can be seen that the wall has
The effect of heat losses in reverse combustion experiments

Figure 5.12: The effect of an adiabatic reactor wall (case 4) on \( m_{su} \) (Solid line). Reference results: 2-D adiabatic simulation with \( \Delta R_w \to 0 \) cm.

two effects: (1) the temperature behind the reaction front decreases due to the heat capacity of the wall and (2) preheating via the reactor walls causes bending of the isotherms near the tube walls. It can be observed that for with an increased radius of the reactor, the curvature of the reaction front becomes less. In addition, the decrease of the temperature behind the reaction front becomes less.

The ignition rate as a function of reactor radius \( R_i \) and wall thickness \( \Delta R_w \) is presented in Fig. 5.14. The curve obtained for variation of \( R_i \) shows that for low values of \( R_i \), \( m_{su} \) is below its adiabatic value. With increasing \( R_i \), \( m_{su} \) increases to a maximum that exceeds the adiabatic value without reactor walls. This is followed by a gradual decrease when \( R_i \) is increased further. The curve obtained for variation of \( \Delta R_w \) shows that for increasing \( \Delta R_w \), \( m_{su} \) increases towards a maximum. Then, a slow decrease follows. Around \( \Delta R = 0.9 \) cm, the ignition rate becomes smaller than the adiabatic value without reactor walls.

The results for \( m_{su} \) as a function of \( R_i \) (cf. Fig. 5.14a) show the effects of preheating via the reactor wall and instationary heating of the reactor wall. For low \( R_i \), \( m_{su} \) is below its adiabatic value. Under these conditions, the ratio of fuel to wall material in a cross-section of the reactor is low, which means that a large share of the heat produced by the conversion reaction is used for the instationary heating of the reactor wall. For larger \( R_i \), \( (R_i \sim 5 - 10 \) cm\)), an increase of \( m_{su} \) above the adiabatic value without reactor walls is observed. In this region, the heat production by the conversion front is larger, which reduces the impact of the instationary heating of the reactor walls. Now, preheating via the reactor walls becomes dominant. If \( R_i \) is increased further, \( m_{su} \) starts to decrease again, because the overall effect of the reactor walls becomes less, because the cross-sectional ratio of fuel to wall material decreases rapidly.

The results for \( m_{su} \) as a function of \( \Delta R_w \) (cf. Fig. 5.14a) show also the effect of instationary heating of and preheating by the reactor walls. For values \( \Delta R_w \lesssim 1 \) cm the preheating effect is dominant, resulting in an increased value of \( m_{su} \). For higher values of \( \Delta R_w \), the instationary heating of the reactor walls becomes dominant, resulting in a lower value of \( m_{su} \).
Figure 5.13: The effect of $r_i$ on $T$ (a,b) and $\dot{q}_p$ (c,d) calculated with 2-D adiabatic simulations with reactor walls (case 4). Left: $r_i = 10$ cm. Right: $r_i = 20$ cm. Isolines at $T = (300 : 100 : 1200)$ K, $\dot{q}_p = (1 : 1 : 3)$ J cm$^{-3}$s$^{-1}$. The highest isoline is printed bold.
The effect of heat losses in reverse combustion experiments

Because the reactor wall can affect the conversion process, it was investigated how the wall conductivity $\lambda_w$ affects the conversion process (cf. Fig. 5.15). It can be observed that for $\lambda_w \lesssim 10^{-2} \text{ J cm}^{-1} \text{s}^{-1} \text{K}^{-1}$, the ignition rate $m_{su}$ is almost independent of $\lambda_w$. For values $\lambda_w \gtrsim 10^{-2} \text{ J cm}^{-1} \text{s}^{-1} \text{K}^{-1}$, $m_{su}$ increases with increasing $\lambda_s$. It becomes larger than the adiabatic value of $m_{su}$ without reactor walls for $\lambda_w \gtrsim 10^{-1} \text{ J cm}^{-1} \text{s}^{-1} \text{K}^{-1}$. Also, these results can be explained by instationary heating and preheating. At low $\lambda_w$, the instationary heating is dominant, while for high values of $\lambda_w$, preheating is dominant. In case the wall conductivity is approximately equal to the conductivity of the fuel bed, i.e. $\lambda_w \sim \lambda_{so}$, the preheating effect is small, while instationary heating of the reactor walls plays a dominant role. In case $\lambda_w = 0.762 \text{ J cm}^{-1} \text{s}^{-1} \text{K}^{-1}$, i.e. for a steel reactor wall, the preheating effect results in a value of 10% difference in $m_{su}$ compared to a value without reactor walls.

The results for adiabatic conversion in a reactor with a metal tube wall presented
Figure 5.16: The combined effect of the reactor walls and heat losses to the environment on \( m_{su} \) for different \( R_w \) (solid line, case 5). Reference results: dashed line: wall effects only (case 4); dashed-dotted line: heat losses to the environment only (case 3).

here show that the presence of reactor walls leads to (1) instationary heating of the reactor walls, resulting in an increased value of \( m_{su} \) and (2) preheating of the unburnt fuel via the walls of the reactor, resulting in a decrease of \( m_{su} \). It is shown that an increased reactor radius reduces the effects of the reactor walls on the conversion process. In addition, it was shown that for a small reactor radius, a wall conductivity smaller than the fuel bed conductivity and a large reactor wall thickness the instationary heating of the walls has a larger effect on \( m_{su} \) than preheating of the unburnt fuels via the walls.

5.3.8 2-D simulations: wall effects and free convection

The results for a non-adiabatic reactor (cf. eg. 5.11) and an adiabatic reactor with steel reactor walls (cf. 5.14) show the separate effects of heat losses and reactor walls on \( m_{su} \). To observe a situation where the combined effect is present, a simulation was performed for a reactor with steel walls directly exposed to free convection.

Results for the combined effect of heat losses to the environment and wall effects are presented in Fig. 5.16. It can be observed that for \( R_i < 15 \text{ cm} \), an uninsulated reactor with a steel wall causes the largest deviations in \( m_{su} \). For \( R_i > 15 \text{ cm} \), there is no configuration that results in a significant deviation of \( m_{su} \) compared to other configurations, although the use of an insulated reactor with steel tube walls results in the smallest deviation.

5.4 Discussion of experimental and numerical results

The experimental and numerical results presented in this study show that heat losses can have a significant effect on the determination of the ignition rate in an experimental setup. The experimental results (cf. Fig. 5.6 show that the three differ-
ent heat loss mechanisms that were identified can lead to deviations of about 10% for the conditions studied. The overview of model results (cf. 5.16) shows that even for larger reactor radii \( R_i > 20 \text{ cm} \) these effects lead to deviations of about 10% in \( m_{sw} \). In the introduction, it has been pointed out that errors of about 10% are present between different numerical models. Therefore, either the heat losses have to be accounted for in the 1-D models or the experimental setup has to be optimized to reduce their impact.

A comparison between the description of heat losses to the environment with a 1-D and 2-D model approach shows that it is difficult to represent this type of heat losses accurately in a 1-D model. The volumetric heat loss term in such a model can only be used to obtain for a first estimation and to obtain insight in the effect of heat losses on the spatial profiles of the conversion front and the main conversion parameters \( m_{sw}, T_f \) and \( \epsilon_b \). The radial transport of heat introduces an additional time and length scale in the problem which is not accounted for in the 1-D approximation. The fact that at the centerline of the fuel layer the effect of heat losses is noticed only indirectly cannot be represented by a 1-D model. Furthermore, it has been shown that the effect of the presence of a wall in the reactor results in instationary heating of the reactor walls and preheating of the wall. The inclusion of a term in the 1D model to include the instationary heating of the reactor walls (cf. [30]) represents only part of the effects of a reactor wall, because it does not account for the preheating effect.

The model results show that an insulated reactor with a thin wall made of a material with a low value of \( c_p, \lambda_w \lesssim \lambda_{s0} \), a large radius \( R_i > 20 \text{ cm} \) reduces the effect of heat losses. However, this means that a wall material has to be found that combines these properties and that, in addition, has the property that it sufficiently strong to deal with strong temperature gradients, has a high melting point and is sufficiently strong to make it possible to use a thin reactor wall. Ceramic materials could be used because they have a low thermal conductivity. Values as low as \( \lambda = 1.5 \times 10^{-2} \text{ J cm}^{-1}\text{s}^{-1}\text{K}^{-1} \) have been reported for Zirconium ceramics [113].

5.5 Conclusions

In this paper, a numerical and experimental study of heat losses in reverse fixed bed combustion has been presented. The adiabatic value of ignition rate is the main quantity to validate advanced 1-D conversion models. It is shown that heat losses may contribute to errors of \( \sim 10\% \) in the ignition rate. Because the difference in the predicted values of the ignition rate by advanced conversion models is of the same order of magnitude, the results of this paper show that reduction of the effect of heat losses is important for model validation.

The experiments with a quartz and steel reactor wall have shown that for steel, a material with a higher conductivity than quartz, an increased value of the ignition rate is observed due to increased conduction of heat via the tube walls. In addition, a comparison between an insulated and an non-insulated reactor with a steel reactor wall shows that applying insulation leads to in increased ignition rate. For high values of the air flow, this effect was significant. For low values of the air flow, the reproducibility of the measurements could be investigated further to find out if a
significant effect can also be observed. Furthermore, for an insulated reactor with a steel reactor wall, it was observed that the ignition rate did not reach a stationary value due to the effect of preheating of the unburnt fuel by conduction via the tube walls.

The numerical study shows that the effect of heat losses can be described qualitatively with a 1-D model that incorporates an effective volumetric heat loss term. However, by using such a term, the effect of heat losses is overestimated. Thus, for more quantitative predictions, a 2D model approach should be used.

Simulations on a 2-D set of model equations were used to investigate the effect of three heat loss mechanisms, i.e. heat loss to the environment, instationary heating of the reactor walls and preheating of the unburnt fuel via the reactor wall. Heat losses affect the time between ignition and the time before a stationary front is obtained and therefore influence the choice for the height of the reactor. Furthermore, it is shown that heat losses to the environment and to the reactor walls is reduced when the radius of the reactor is increased. The effect of instationary heating of the reactor walls and preheating of the unburnt fuel via the reactor walls decreases if the thickness of the wall is reduced.

The 2-D simulations also indicate that the effect of the reactor wall on the conversion process can be reduced by choosing a material with a low specific heat and a low conductivity. A low specific heat reduces the effect of instationary heating of the reactor walls. Choosing a wall material with a conductivity smaller than the conductivity of the fuel layer strongly reduces the preheating effect.

The work presented in this paper will be extended in two directions. Firstly, a reactor with a sufficiently large radius \( r \sim 20 \text{ cm} \) and an insulated reactor wall of a ceramic material will be developed. Secondly, the 2D conversion model will be improved (e.g. by including radiation) and will be written down in a dimensionless formulation. A dimensionless formulation will give better insight in the important length and time scales of the conversion process and can be used to present a generally valid expression for the deviations in the ignition rate as a function of reactor properties.
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Chapter 6

Detailed chemistry for NO\textsubscript{x}-predictions

6.1 Introduction

Grate furnace combustion of biomass for energy production can play a significant role in the reduction of greenhouse gas emissions because biomass is a renewable energy source. However, the emissions of NO\textsubscript{x} during grate furnace combustion are an important drawback of this conversion technique because of the environmental problems this entails, for example acid precipitation and smog [14]. The main cause of the NO\textsubscript{x} emissions is the oxidation of nitrogen present in the solid fuel, so-called fuel-N [13]. In this chapter, a model is described that can be used to study the evolution of the fuel-N during the conversion process on the grate. Such a model can be serve as part of an overall CFD (Computational Fluid Dynamics) model for grate furnace combustion. This overall model can then be used to study the NO\textsubscript{x}-emissions of grate furnaces as a function of operating conditions, grate furnace design parameters and fuel properties.

Several stake-holders can benefit from the development of a model to describe NO\textsubscript{x} formation in grate furnaces. Engineering firms that design grate furnaces can use the model to optimize the operation and design of these furnaces to help operators to meet the emission regulations. Operators of optimized grate furnaces can use woody fuels with a higher nitrogen content, for example fibreboard or MDF. (The high content of fuel-N is caused by chemical binders in chemical binders [31]). This leads to two economic advantages for operators: (1) increase fuel flexibility, i.e. reduces operator dependency on a limited number of fuels, and (2) lower costs compared to using fuels with a low N-content, i.e. fresh wood. In turn, these advantages will lead to a wider application of grate furnace combustion by operators. For society, the wider application of biomass conversion contributes to the reduction of CO\textsubscript{2}-emissions. In addition, society can also benefit from the cost reductions.

The focus of this paper is on the release of fuel-N in the solid fuel layer, because this is the root cause of the NO\textsubscript{x} formation. Grate furnace combustion consists of two steps: (1) on the grate, conversion of the solid fuel into gases takes place and (2) above the solid fuel layer, secondary air is supplied to burn out the gases. The NO\textsubscript{x} formation takes place by release of the fuel-N during the conversion on the grate,
mainly in the form of the species NH$_3$ and HCN, while above the solid fuel layer, part of these species is oxidized to NO, causing the NO$_x$-emissions.

The release of N-compounds by the solid fuel is dependent of three processes (1) the main parameters of the conversion process, i.e. the temperature and conversion rate, (2) the kinetics of the release mechanism and (3) heterogenous and homogenous reactions of the N-precursors in the void space in the bed. The conversion process creates the conditions for the release of the N-species, while the release mechanism determines the rate of the N-release and the distribution over the precursors given these conditions. The homogenous and heterogenous reactions govern the further evolution of the precursors in the fuel layer.

The conversion process of the fuel layer is a reverse combustion process [35], in which a conversion front propagates through a porous fuel layer of wood particles in the opposite direction of the air flow. When the conversion front passes, individual fuel particles undergo a devolatalization process and a gasification process. At low air flow rates, char is left behind the conversion front due to incomplete conversion. When the conversion front reaches the bottom of the fuel layer, burnout of the char that accumulated on top of the front takes place. [16]. Generally, 1-D (one-dimensional) models (cf. e.g. [28, 30, 39]) are used to describe the conversion process on the grate. The 1-D approach is a good approximation. The predictions for the velocity of the conversion front velocity results in differences of only $O(10\%)$ with experiments [40], which is quite good given the many parameters in the models.

Investigation of the release of N-precursors in solid fuel fired systems has shown that it is dependent of the conversion process (pyrolysis, char burnout) and that it is a function of particle properties (size, chemical composition) and conversion conditions (conversion rate, heating rate, temperature) [25]. During the devolatalization process, fuel nitrogen is distributed over tars, gasses and char The main gaseous nitrogen compounds (or so-called N-precursors) are NH$_3$ and HCN. Higher heating rates and smaller particles result in a higher ratio of HCN over NH$_3$. During the char burnout process, NO is the main product. In addition, it was observed that heterogenous reactions of NO with char can lead to the formation of N$_2$.

Measurements of the release of nitrogen in a conversion front by Samuelsson [32] indicate that this is a complex process because in the front, pyrolysis, (partial) oxidation of the pyrolysis products and partial oxidation of the solid fuel take place simultaneously. Measurements with sawdust pellets and bark pellets show that in the oxygen-rich part of the conversion front (upstream side), the major nitrogen compound in the gas phase is NO, i.e. the N-precursors are directly converted into NO. In the fuel rich part (at the downstream side) the main N-compound is NH$_3$, i.e. a large part of the NO produced in the oxygen rich part of the reaction zone is converted back into NH$_3$.

The measurements of Samuelsson also show that the overall conversion of fuel-N during the front propagation phase is dependent of operating conditions and fuel type. For the sawdust pellets, the fraction of fuel-N (i.e. fuel nitrogen) that is converted into N$_2$ is the largest with ($O(60\%)$) for various air velocities. The fractions of fuel-N that are converted into NH$_3$ and tar-N are ($O(30\%)$) and ($O(20\%)$) respectively. With increasing air ratio, the fuel-N converted to NH$_3$ decreases while the conversion into N$_2$ increases. For measurements with bark pellets, the observed
trends were the same but the amount of fuel-N converted into N\textsubscript{2} was lower, while the conversion into Tar-N and NH\textsubscript{3} was higher.

Experimental results with different fuels by others are qualitatively in agreement with the results of Samuelsson. Weissinger [31] shows that NH\textsubscript{3} is also the main precursor in case of fibreboard, a fuel with a high nitrogen content (3.4 Wt\%) due to the presence of a chemical binder. Experiments with straw by Van der Lans et al. (cf. [27]) show that the product gas composition contained 12\% of NH\textsubscript{3} and 4\% NO during the conversion process.

Despite the accurate results for predictions of the conversion front velocity obtained with 1-D models, the description of the N-compounds in the reaction zone is limited. In most model studies, the evolution of N-compounds is not discussed (cf. e.g. [28,30,39]). In other studies, a course representation of the evolution of the nitrogen species is represented. In the study of Van der Lans et al. [27] a model for reverse combustion is described, but to draw conclusions about the fate of the fuel-N, experimental data is used in combination with the assumption that the release of fuel-N is proportional to the conversion rate of carbon. In the study of Zhou et al. (cf. [114]) concentrations of nitrogen compounds in the gas phase are predicted, but a fixed distribution for the partitioning of the fuel nitrogen over the tar, char and gas is used. Also, the distribution of the fuel-N in the gas over the N-precursors is fixed. In the study of Khor et al. [115] all fuel-N is released as NH\textsubscript{3} and a simplified kinetic model (the De Soete-model, (cf. [54])) consisting of two rate expressions for the formation of NH\textsubscript{3} into NO and N\textsubscript{2}, respectively.

In this chapter, a 1-D model is presented that can be used to predict the formation of N-precursors in a solid fuel layer. In order to predict the main parameters of the conversion process (temperature, conversion rate) conservation equations for the solid phase and the gas phase are used. The release of N-compounds and other chemical species is included by using a lookup table (LT) in which experimental data for the release of 17 gas phase including three N-precursors as a function of temperature and conversion of biomass is used [72,116]. By using a LT, a limited set of experimental data can be used to obtain model predictions for a wider range of conditions. The evolution of the N-compounds and the other gas phase species is described with detailed kinetic mechanisms that were previously used mainly for gas phase combustion. With this model approach, all phenomena related to the formation of nitrogen species are included. The inclusion of release rates of various chemical species by means of an LT approach and the application of detailed gas phase kinetic mechanisms has not yet been applied in other studies.

It is the main goal of this paper to outline the structure of the model and to show that all processes relevant for N-predictions are represented. In order to meet this goal and to facilitate the computations, a minimal set of data is used. This means that the evolution of the main gas phase species is taken into account in the model, while the evolution of the tars originating from the solid fuel is not yet represented. Instead of the most elaborate mechanism for biogas conversion currently available (cf. [24]) a reaction mechanism for natural gas combustion (with N-functionality) is used (GRImech3.0, cf. [78]) because it comprises less species and reactions. Furthermore, only one heterogenous reaction for char conversion (i.e. between char and oxygen) is included, while this process involves multiple heterogenous reactions.
Detailed chemistry for NO\textsubscript{x}-predictions

(e.g. with carbon dioxide, steam and nitrogen oxide).

A secondary goal of this chapter is to show the two main advantages of using a LT approach. Firstly, using a representation of release rates by a LT enables to increase the accuracy of the model by adding more data directly obtained from experiment to the table (i.e. without the need for fitting or further modeling) for species release rates, but also for e.g. the solid enthalpy of formation. Secondly, it provides a framework to develop a coherent data set for the conversion of a ‘unit’ of biomass that can also be used in other models, e.g. single particle models or models for fluidized bed combustion.

The further outline of this chapter is as follows. First, the governing equations of the model are presented (Sec. 6.2). Then, an initial test of the model structure for coal conversion is presented (Sec. 6.3). In this test, coke is used as a fuel because this result in an LT that is less complex that for woody biomass. Subsequently, the LT approach for woody biomass is introduced (Sec. 6.4). Then, the results of the model for biomass conversion are presented (Sec. 6.4.4) and it is described how it can be extended (Sec. 6.5). The chapter ends with conclusions (Sec. 6.6).

6.2 Governing equations

In chapter 3 of this thesis a global overview of the model equations has been given. In this section, it is described how this set of equations is used here in a 1-D configuration. The equations for the solid phase are described first because the conversion of the solid fuel is the first step of the reverse combustion process. The equations for the gas phase, where burnout of the species released by the solid fuel takes place, is described subsequently.

6.2.1 Solid phase

First, we discuss the conservation equations for the solid phase. The continuity equation for the solid mass is given by

$$\frac{\partial}{\partial t}((1 - \epsilon) \rho_s) = \sum_{i_s} \dot{\omega}_{gs}^{i_s} + (1 - \epsilon) \sum_{i_s} \dot{\omega}_{s}^{i_s}.$$  \hspace{1cm} (6.1)

Here, the term on the left hand side is the time-dependent term, while the right hand side contains the mass source term. The porosity is indicated with \(\epsilon\), the solid density by \(\rho_s\), while the source terms of solid species \(i_s\) due to heterogenous and homogeneous reactions are indicated by \(\dot{\omega}_{gs}^{i_s}\) and \(\dot{\omega}_{s}^{i_s}\) respectively. The heterogenous source terms are indicated with the superscript \(gs\), because in these reactions, species from both the gas and solid phase are involved. The homogenous source terms are indicated with the superscript \(s\), because only species of the solid phase are involved in these reactions. The conservation equations for the solid phase species \(Y_{i_s}\) read:

$$\frac{\partial}{\partial t}((1 - \epsilon) \rho_s Y_{i_s}) = \dot{\omega}_{gs}^{i_s} + (1 - \epsilon) \dot{\omega}_{s}^{i_s}.$$  \hspace{1cm} (6.2)
6.2 Governing equations

In this study, a formulation of conservation of energy in terms of the enthalpy is used. For the solid phase enthalpy $h_s$ this equation reads

$$\frac{\partial}{\partial t} \left( (1 - \epsilon) \rho_s h_s \right) - \frac{\partial}{\partial x} \left( \frac{(1 - \epsilon) \Lambda}{c_{ps}} \frac{\partial h_s}{\partial x} \right) = -\dot{\omega}_h^{gs}. \quad (6.3)$$

Here, the terms on the left hand side are related to unsteady effects and dispersion respectively. The right hand side contains the source term. In this equation, $\Lambda$ is an effective heat dispersion coefficient for the gas-solid system, $c_{ps}$ is the specific heat of the solid material and $\dot{\omega}_h^{gs}$ is the enthalpy source term due to heterogenous reactions. The enthalpy source term is given by

$$\dot{\omega}_h^{gs} = \sum_{i_g} h_{i_g} \dot{\omega}_{i_g}^{gs} + k (T_s - T_g). \quad (6.4)$$

The first term on the right hand side represents the enthalpy due to the exchange of species between the two phases, while the second term describes the exchange of heat. A further description of the enthalpy source term is presented in Appendix A.

The enthalpy of the solid phase is given by

$$h_s = \int_{T_0}^{T_s} c_{ps}dT_s' + h_0^s, \quad (6.5)$$

where $h_0^s$ is the enthalpy of formation of the solid and $T_0$ the reference temperature. The quantities $c_{ps}$ and $h_0^s$ are effective quantities, because they could be specified in more detail by writing them in terms of $c_{pi_s}$ and $h_0^i_s$, i.e. the specific heat and enthalpy of formation of the individual solid species $i_s$.

6.2.2 Gas phase

For the gas phase, a similar set of equations can be written. The conservation equation for the gas phase is given by:

$$\frac{\partial}{\partial t} \left( \epsilon \rho_g \right) + \frac{\partial}{\partial x} \left( \epsilon \rho_g v_g \right) = \sum_{i_g} \dot{\omega}_{i_g}^{gs}. \quad (6.6)$$

Here, the left hand side contains a transient term and a convective term, the right hand side contains the source term. In this equation, $\rho_g$ is the gas density, $v_g$ the interstitial gas velocity and $\dot{\omega}_{i_g}^{gs}$ the reaction source term of gaseous species $i_g$ due to homogenous reactions. From mass conservation, it follows that

$$\sum_{i_g} \dot{\omega}_{i_g}^{gs} = - \sum_{i_s} \dot{\omega}_{i_s}^{gs}. \quad (6.7)$$

The conservation equations for the gas mass fractions $Y_{i_g}$ are given by

$$\frac{\partial}{\partial t} \left( \epsilon \rho_g Y_{i_g} \right) + \frac{\partial}{\partial x} \left( \epsilon \rho_g v_g Y_{i_g} \right) - \frac{\partial}{\partial x} \left( \rho_g D \frac{\partial Y_{i_g}}{\partial x} \right) = \dot{\omega}_{i_g}^{gs} + \epsilon \dot{\omega}_{i_g}^{g}. \quad (6.8)$$
with the left hand side a transient term, convective term, and dispersive term and on the right hand side source terms related to heterogeneous (superscript \(g_s\)) and homogenous gas phase reactions (superscript \(g\)) respectively. In the dispersive term, \(D\) represents the effective mass dispersion coefficient. The enthalpy equation for the gas phase is given by

\[
\frac{\partial}{\partial t}(\epsilon \rho_g h_g) + \frac{\partial}{\partial x}(\epsilon \rho_g v_g h_g) - \frac{\partial}{\partial x} \left( \epsilon \Lambda \frac{\partial h_g}{\partial x} \right) = \dot{\omega}_g^{g_s}.
\] (6.9)

with transient, convective and dispersive terms on the left hand side and a source term on the right hand side. The enthalpy of the gas phase is given by

\[
h_g = \sum_{i_g} Y_{i_g} h_{i_g}
\] (6.10)

with

\[
h_{i_g} = \int_{T_0}^{T} c_{p_{i_g}} dT + h_{i_g}^0,
\] (6.11)

where \(h_{i_g}^0\) is the enthalpy of formation of the gas phase species \(i_g\).

For the dispersive terms in the conservation equations for enthalpy and species, effective coefficients \(\Lambda\) and \(D\) are used. For the dispersion term in the species equation (Eq. 3.7) this means that \(\epsilon\) is not represented. The presence of \(\epsilon\) in the porosity in the enthalpy equations (Eqs. 6.9, 6.3) results from the fact that \(\Lambda\) is a coefficient for dispersion of heat by both the gas and the solid phase. A fraction of \((1 - \epsilon)\) of the transport takes place through the solid phase, while a fraction \(\epsilon\) takes place by the gas phase.

### 6.2.3 Data for model coefficients

The data required to solve the model consists of the physical data for the solid properties and the transport coefficients, the kinetic data needed to describe the heterogeneous and homogenous processes in the fuel layer and the physical data for the gas phase species.

The physical data for the solid material and the transport coefficients are based on a coal fuel bed. It concerns the specific heat of the solid, the solid density (which is assumed to be constant) and the effective dispersion coefficients for heat and mass. For these properties, data has been presented in section 4.2.3.

The data for the chemistry is related to the heterogeneous and the homogenous processes. For the heterogeneous reactions related to the pyrolysis process, a LT approach is used. The principle of this approach is described in Sec. 6.3.1 for the initial tests with coal and in Sec. 6.4 for biomass. For the homogenous reactions in the coal bed, the skeletal mechanism of Smooke [76] is used. For the homogenous reactions in the biomass fuel bed, the GRImech3.0 mechanism (cf. [117]) is used. This mechanism is optimized for the combustion of natural gas and contains a subset of reactions to describe the nitrogen evolution in this combustion process. The mechanism consists of 53 species and 325 reactions.
The physical data for the properties of the gas phase species pertains to the data required to determine $c_{pi,g}$ and the $h_{i,g}$. To determine this data, polynomial correlations are used that are supplied together with the reaction mechanism GRImech3.0.

### 6.3 Model validation for a coal bed

This section describes a test of the model structure for a fuel layer of coke. Using coke has the advantage that there is only one solid phase species, pure carbon, which reduces the amount of gas phase species and chemical reactions. This means that separate species equations for $Y_{is}$ (cf. Eq. 6.2) are not solved. In this section, an expression for the reaction source term is introduced first (Sec. 6.3.1), followed by a further specification of the solid phase enthalpy (Sec. 6.3.2). After this, it is described how the model equations are solved 6.3.3. Finally, model results are presented (Sec. 6.3.4).

#### 6.3.1 Heterogeneous reaction source terms

In this section, the LT for the heterogeneous reaction source terms $\omega_{gs}^i$ and $\omega_{gs}^j$ is described. These source terms are given as a function of the lookup variables $\chi_i$ by

$$\omega_{gs}^i = \omega_i (\chi_i), \quad (6.12)$$

where the index $i$ runs over both the gas phase species $i_g$ and the solid phase species $i_s$. The LT is constructed in a preprocessing step. During simulations, it is used to retrieve the values for the source terms as a function of the discrete values for $\chi$ by means of an interpolation routine. For the conversion of coal, a single step reaction is used, i.e.

$$C + \sigma O_2 \rightarrow \sigma CO CO. \quad (6.13)$$

In writing down this reaction, it is assumed that the gas phase product of the heterogeneous combustion process is CO (as opposed to $CO_2$ used in Chapter 4. The CO will oxidize rapidly to $CO_2$ in the gas phase. Then, the $\omega_{gs}^i$ that are non-zero are given by

$$\omega_{O_2}^{gs} = -\sigma_{O_2}^{gs} R, \quad \omega_{CO}^{gs} = +\sigma_{CO}^{gs} R \quad (6.14)$$

and the $\omega_{gs}^i$ by

$$\omega_{C}^{gs} = -R \quad (6.15)$$

with the source term $R$ given by.

$$R = \frac{1}{k_r^{-1} + k_m^{-1}} S_u \left( \frac{1 - \epsilon}{1 - \epsilon_u} \right)^{2/3} \rho_g Y_{O_2} \quad (6.16)$$

where $k_r$ is the Arrhenius rate constant, $k_m$ the mass transfer coefficient, $S_u$ the specific surface area of the fuel bed per unit volume. A further explanation of the source term has been presented in Chapter 4 in Sec. 4.2.3. Here, we note that although the temperature is not explicitly present in the expression for the source term 6.16, it is implicitly dependent on the temperature via $k_r$ and $k_m$. In the implementation of
the equations, the solid temperature $T_s$ is used for this. The dependencies of $R$ are then given by

$$ R = R(T, Y_{O_2}, \epsilon) \quad (6.17) $$

Thus, a LT can be constructed on the basis of Eqs. 6.14-6.16 that specifies the source terms $\omega^{gs}_{O_2}$, $\omega^{gs}_{CO}$ and $\omega^{gs}_C$ as a function of three lookup variables: $\chi_1 = T, \chi_2 = Y_{O_2}, \chi_3 = \epsilon$.

It should be noted that for coal, the use of a lookup table in principle not different from using a functional expression for the reaction source term in the numerical code. If a straightforward expression for the reaction source term is available like Eq. 6.16, it offers no specific advantages. However, the availability of such an expression makes it possible to validate the implementation of the LT, which is the purpose of the simulations with coal.

### 6.3.2 Solid phase enthalpy

For the enthalpy equation, the enthalpy of the solid phase $h_s$ needs to be specified. This involves specification of $c_{ps}$ and $h^0_s$. For $c_{ps}$, a constant value is assumed. Then, the original expression for $h_s$ given by Eq. 6.5 reduces to

$$ h_s = c_{ps}(T - T_{ref}) + h^0_s. \quad (6.18) $$

The standard enthalpy of formation of the solid $h^0_s$ can be derived from the standard enthalpy of combustion $\Delta h^0_r$. This method is chosen because $\Delta h^0_r$ can be determined easily by means of standard experimental equipment like a bomb calorimeter. Although in the model, it is assumed that the coal consists of pure carbon, a general derivation of the method to obtain $h^0_s$ from $\Delta h^0_r$ is presented here. The derivation starts with writing the conversion of a solid fuel of a general composition:

$$ \sigma_F C Z_{C} H Z_{H} O Z_{O} + \sigma_{O_2} O_2 \rightarrow \sigma_{CO_2} CO_2 + \sigma_{H_2O} H_2O. \quad (6.19) $$

Here, the $Z_{i_e}$ indicate molar fractions of the elements in the wood, where $i_e$ is an index running over the elements. The $\sigma$’s are mass based stoichiometric coefficients given by

$$ \sigma_F \quad = \quad 1, \quad (6.20) $$

$$ \sigma_{O_2} \quad = \quad \left( \frac{Z_C}{M_C} + \frac{1}{4} \frac{Z_H}{M_H} - \frac{1}{2} \frac{Z_O}{M_O} \right) M_{O_2}, \quad (6.21) $$

$$ \sigma_{CO_2} \quad = \quad \frac{Z_C}{M_C} M_{CO_2}, \quad (6.22) $$

$$ \sigma_{H_2O} \quad = \quad \frac{1}{2} \frac{Z_H}{M_H} M_{H_2O}. \quad (6.23) $$

The elemental mass fractions in the solid $Z_{i_e}$ are related to the values $X_{i_e}$ by

$$ Z_{i_e} = \frac{X_{i_e} M_{i_e}}{\sum_{i_e} X_{i_e} M_{i_e}}; \quad X_{i_e} = \frac{Z_{i_e}}{M_{i_e} \sum_{i_e} \frac{Z_{i_e}}{M_{i_e}}}. \quad (6.24) $$
For pure carbon, $X_C = 1$, $X_H = 0$. In terms of standard enthalpies, the reaction enthalpy is given by

$$\Delta h^0_r = \sum_{i_p} \sigma_{i_p} h^0_{i_p} - \sum_{i_r} \sigma_{i_r} h^0_{i_r}$$

(6.25)

Thus, for coke, the standard enthalpy can be obtained from

$$\Delta h^0_r = \sigma_{CO_{2}} h^0_{CO_{2}} - \sigma_{\text{coke}} h^0_{\text{coke}} - \sigma_{O_{2}} h^0_{O_{2}}$$

(6.26)

Using $\Delta h_r = -28.9 \times 10^3 \text{ J g}^{-1}$ [16], $\sigma_{CO_{2}} = 3.67$, $h_{CO_{2}} = 8.94 \times 10^3 \text{ J g}^{-1}$ and $h_{O_{2}} = 0 \text{ J g}^{-1}$ results in $h^0_s = -3.9 \times 10^3 \text{ J g}^{-1}$. The species source terms can also be used in the source term for the enthalpy equation, $\sum_{i_g} h_{i_g} \omega_{i_g}^{gs}$. Together with the values for $h_{i_g}$ computed by the numerical simulation, this completely specifies the enthalpy source term.

### 6.3.3 Solving the model equations

For the simulations with coal, solid phase equations given by Eqs. (6.1) and (6.3) are solved, while for the gas phase Eqs. (6.6)-(6.9) are solved. In the model, it is assumed that the coal consists entirely of pure carbon. This is a good approximation for coals with a low volatile content. Because then there is only a single solid phase species, the equations for $Y_{i_s}$ do not need to be solved. In this case, Eq. (6.1) can be considered as an equation for the porosity. The density $\rho_{s0}$ is constant and the porosity is a variable, following the shrinking core model introduced in Chapter 4, Sec. 4.2.3.

For the homogeneous gas phase reactions, detailed kinetic mechanisms are used. The mechanism of Smooke [76] for methane combustion is used to test whether detailed kinetic mechanisms can be used. It is a skeletal mechanism, i.e. it consists of a minimal set of species (16) and reactions (25) necessary to describe methane combustion.

The equations have been implemented in the reactive flow solver Chem1D [98], which uses a finite volume method in combination with a modified Newton procedure to solve the equations. A linear interpolation routine is used to determine $R$ as a function of $T$, $Y_{O_2}$, $\epsilon$.

### 6.3.4 Results

The results presented in this section are generated by using the implementation of the general model equations presented in Sec. 6.2 for coal, as described in Sec. 6.16,6.3.2 and 6.3.3. The main goal of the presentation of the results is to illustrate that the model approach is functioning properly. For this purpose, spatial profiles of model variables, fluxes of mass and enthalpy and the dependence of main combustion process parameters ($m_{su}$, $T$) are presented.

Spatial front profiles of the temperatures, reactants and products for a steady conversion process (cf. Fig. 6.1) show that the model can resolve the reaction layer in detail. In Fig. 6.1a, it can be seen that initially, $T_s$ and $T_g$ are close to $T_u$. The increase of both temperatures marks the location of the front. Behind the front, $T_s$
and \( T_g \) approach the adiabatic flame temperature \( T_b \). The difference between \( T_s \) and \( T_g \) over the largest part of the domain is small. The region where a difference is present is near the maximum temperature. At this location, the reaction source term is the largest (cf. Fig. 4.3, implying a rapid production of heat in the solid phase that is transferred to the gas phase more gradually.

The profiles of the oxygen and the porosity 6.1b show an increase and decrease respectively at the location of the reaction front. The profile of CO, the species released by the solid phase, shows a maximum with increasing \( x \) first. After the minimum that follows, a slow increase is observed.

The decrease of \( Y_{O_2} \) and the increase of \( \epsilon \) can be explained by the consumption of \( O_2 \) and solid material by the reaction. The initial maximum in the CO concentration can be explained in terms of the rates of the heterogenous reaction and the homogenous reactions. At low \( T_s \) (at the unburnt side of the reaction zone), the release of CO already starts, while \( T_g \) is still too low for a rapid oxidation by the homogeneous gas phase reactions. At higher temperatures, the rate of the homogenous oxidation reaction is increasing faster than the rate of the heterogenous process. This means that at higher \( T \), \( Y_{CO} \) is decreasing. The maximum \( Y_{CO} \) marks the transition between these two regions. The gradual increase of \( Y_{CO} \) at the end of the domain can be explained in terms of the equilibrium between CO and \( CO_2 \). The higher temperatures and lower oxygen concentrations in this region compared to the conditions in the center of the reaction zone result in a small \( Y_{CO} \) at the burnt side.

Spatial profiles of the mass flows and enthalpy flows (cf. Fig. 6.2) illustrate that mass and enthalpy are conserved in the computations. It can be seen that \( m_s \) decreases during the conversion process, while \( m_g \) increases. The total mass flow \( m_t \) is constant. The enthalpy flows \( \phi_{hs} \) and \( \phi_{hg} \) for solid and gas show a maximum as a function of the spatial coordinate \( x \). The same holds for the total enthalpy flow \( \phi_{ht} \).

The decrease of \( m_s \) and the increase of \( m_g \) can be explained by the transfer of mass from the solid phase to the gas phase due to the heterogenous chemical reaction. The constant value of \( m_t \) indicates that the total mass is conserved. The

![Figure 6.1: Combustion process parameters as a function of \( x \). Left: \( T_s \) and \( T_g \). Right: \( \epsilon \), \( Y_{O_2} \), \( Y_{CO_2} \) and \( Y_{CO} \). Results for a coal bed obtained with the mechanism of Smooke. [76].](image-url)
maxima in $\phi_{hs}$ and $\phi_{hg}$ are caused by the difference in the length scales of spatial variation of the temperature (preheat zone) and the progress of the reaction (reaction zone) that results in preheating of the unburnt fuel at the unburnt side of the reaction front. In the preheat region, the combination of unreacted fuel and oxidizer with elevated temperatures causes the maxima in $\phi_{hs}$ and $\phi_{hg}$. This also explains the maximum in $\phi_{ht}$, because $\phi_{ht} = \phi_{hs} + \phi_{hg}$. The so-called excess enthalpy in the reaction zone was also observed by others (cf. e.g. [118]). The fact that $\phi_{ht,b} = \phi_{ht}$ shows that over all, enthalpy is conserved.

With the model, the velocity and temperature of the reaction front can be calculated as a function of the gas mass flow $m_{gu}$ (see Fig. 6.3). These curves were already described and explained in Chap. 1. Here, we restate that the behavior of $T_b$ and $m_{su}$ near $m_{gu} = 0$ and the extinction limit $m_{gu,E}$ are not reached completely due to numerical difficulties. A description of this results illustrate that with the full version of the model equations and using a manifold for the reaction source term, the combustion process can be described properly.

### 6.4 Lookup Table for biomass

To use the model equations presented in Sec. 6.2 for biomass conversion, the source terms $\omega_i^{gs}$ have to be specified. In this section, it is described how a lookup table can be generated to do this. It starts with a description of the method that is used to construct the LT. This is followed by a discussion of the implementation based on experimental data.

![Figure 6.2: Conservation of mass and energy. Left: mass flows $m_s$ and $m_g$ and total mass flow $m_t$. Right: enthalpy flows $\phi_{hs}$, $\phi_{hg}$ and total enthalpy $\phi_{ht}$. The dotted line indicates the magnitude of $\phi_{ht}$ far from the reaction zone.](image)
6.4.1 Method

The conversion of biomass in a solid fuel layer is a complex process because it consists of three main phenomena that partially occur simultaneously: devolatalization, conversion of the volatiles and conversion of the char. The conversion of the volatiles can be described with gas phase kinetics and is therefore not part of the LT. The char conversion is also not a part of the LT, because it can be described with the functional form presented in Eq. (6.16), i.e. a LT approach is simply not needed. To formally split of the char conversion from the heterogeneous processes, we separate the heterogeneous source terms \( \omega_{gs} \) in terms for devolatalization (superscript \( D \)) and char conversion (superscript \( C \)). This can be written down explicitly as

\[
\omega_{gs} = \omega_{gs,D} + \omega_{gs,C}
\]  

(6.27)

The source terms specified in Eqs. (6.15)-(6.16) are used to represent \( \omega_{gs,C} \).

Biomass conversion experiments with a TAG-FIR (Thermo Gravimetric Analysis - Fourier Transform Infrared Spectroscopy) apparatus [72, 116] are used in this chapter for the further specification of the source terms \( \omega_{gs,D} \). In such an experiment, the conversion of the wood is controlled by applying a desired temperature profile \( T(t) \) to a microscopic sample of pulverized wood placed in a reactor flushed with an inert gas. The thermogravimetric analysis is aimed at determining the conversion rate by recording the mass \( m(t) \) of the sample during the conversion process. For this, the reactor is placed on a mass balance. The Fourier transform infrared spectroscopy is aimed at determining the composition of the released volatiles. For by means of a mass balance on which the sample is placed. This is done by leading the inert gas flow together with the volatiles along the FTIR detector. From the experiment, the

![Figure 6.3: Main combustion process parameters as a function of \( m_{gu} \). Left: solid mass flow \( m_{su} \). Right: Gas temperature at the burnt side.](image)
source terms

\[ \omega_{i_g}^{gs,D} = \rho_{s0} \frac{dy_{i_g}}{dt}. \] (6.28)

are derived. Here, \( \rho_{s0} \) is the original density of the solid and \( y_{i_g} \) the mass fraction of the solid material that is converted into gas phase species \( i_g \).

To use the results of TGA-FTIR experiments in the LT, the results of the experiments have to be casted in the form

\[ \omega_{i_g}^{gs,D} = \omega_{i_g}^{gs,D}(\chi_i), \] (6.29)

i.e. the lookup variables \( \chi_i \) have to be specified. Because we do not use an underlying model of the conversion process, parameters that are used to control the conversion process or parameters that are determined experimentally can be used. The primary parameter that is used to control the experiment is the temperature of the solid material, \( T_s \). In addition, the heating rate

\[ \mathcal{H} = \frac{dT_s}{dt} \] (6.30)

can be determined from the temperature profile. From TGA-FTIR experiments, it can be concluded that the heating rate has a strong effect on the conversion process, for example on the distribution of volatile matter over tar and gas is. From measurement results presented in Ref. [72] it can be concluded that for a heating rate of 10 K min\(^{-1}\), the gas yield is 49.0 wt% of the original mass of the solid fuel, while for a heating rate of 100 K min\(^{-1}\) the gas yield is only 37.6 wt%.

Parameters that can be determined experimentally are the conversion \( X \), given by

\[ X(t) = \frac{m(t)}{m_0} \] (6.31)

and the elemental composition of the solid, \( Z_{i_e}(t) \). The latter can be determined from the TGA-FTIR experiments if the initial elemental composition of the wood, \( Z_{i_e,0} \), is determined in advance by an elemental analysis method. Then, \( Z_{i_e}(t) \) can be determined by subtracting from \( Z_{i_e,0} \) the elements that leave the solid in the form of gaseous compounds. These gaseous compounds can be detected with TGA-FTIR.

Thus, \( \chi = (T_s, \mathcal{H}, X, Z_{i_e}) \) and the source term can be represented by

\[ \omega_{i_g}^{gs,D} = \omega_{i_g}^{gs,D}(T_s, \mathcal{H}, X, Z_{i_e}) \] (6.32)

It should be noted that \( \chi_i \) ideally is a vector that characterizes the exact state of the solid fuel during the conversion process. Such an exact state consists of all parameters describing the chemical and physical composition of the solid fuel during the conversion process. However, such a description cannot be determined experimentally. It would involve for example the determination of the solid mass fractions of the chemical compounds \( Y_{i_s} \) during the conversion process, which is currently impossible. The vector \( \chi = (T_s, \mathcal{H}, X, Z_{i_e}) \) can therefore be seen as a parametrization of the exact state of the solid fuel in terms of parameters that are experimentally accessible.
The lookup table $\omega_{gs,D}^{t_s}(T_s, H, X, Z_{ie})$ can be generated by performing TGA-FTIR experiments in which the parameters used to control the experiments, $T_s, H$, are varied in ranges that are expected to occur during simulations. The source terms $\omega_{gs,D}^{t_s}$ and the variables $X, Z_{ie}$ can then be determined from the experiments. It can be investigated how the number of measurements used to construct the LT affects the accuracy of the simulations in order to minimize the number of simulations needed in the LT.

There are detailed models for solid fuels, e.g. FG-DVC [72], FLASHCHAIN [119], CPD [120] that in principle could also be used to predict the species release. These models claim to have a good physical and chemical representation of the conversion process and are believed to be able to extrapolate the experimental data to higher heating rates. However, the LT approach that is presented here has three advantages over the detailed models:

- The LT approach is more general than the detailed models for solid fuel conversion, because a LT can be generated on the basis of simulations with these detailed models instead of experimental data.
- The LT approach results in shorter calculation times, because the values for the source terms can be retrieved from a table instead of being calculated online with a complex set of model equations.
- The LT is completely defined by experimental conditions and results. This means that additional data for the characterization of the solid, for example NMR (Nuclear Magnetic Resonance) spectroscopy (cf. [120]) is not necessary.

The claim that the models can be used to extrapolate measurement results to higher heating rates is not supported yet by experimental evidence, while it can be expected that it is difficult. For example, the biomass FG-DVC model uses a fixed end yield of modeled gas phase species, while measurement data indicates that the yields change when the heating rate is varied. Especially when large increases of the heating rate are simulated, this may lead to large deviations in the yields.

In this section, the LT approach has been outlined. It has been shown that only the devolatalization step needs to be incorporated in the manifold. For the source terms related to the devolatalization, TGA-FTIR measurements can be used. From the experiments, also variables can be obtained to parameterize the source terms to construct a look-up table. Finally, it has been shown that the look-up table approach has potentially several advantages over the use of detailed models for the conversion of solid fuels.

### 6.4.2 Construction

In this section, the implementation of TGA-FTIR measurement results of wood pellets of De Jong et al. [72] in a LT is presented. First, an overview of the measurement results of De Jong et al. is given and it is described which measurement results are to be used for the LT. Secondly, it is described how the measurement results are processed to reduce fluctuations in the measurements of the release rates that occur
as a result of an inherently unstable conversion process and imperfect measurement method. The reduction of these fluctuations is performed to prevent numerical difficulties when the data is used in simulations.

**Discussion of TGA-FTIR measurement results**

The experimental results of de Jong et al. [72] consist of \( m(t) \) and \( \omega_i^{gs}/\rho_{s0} \) as a function of \( T \) (cf. Fig. 6.5) and the total yield of char and volatiles (tar, gas) (cf. Tab. 6.2) for \( \mathcal{H} = 10 – 100 \text{ K min}^{-1} \). The experiments of De Jong et al. are used here because they have resulted in one of the most comprehensive and detailed data sets for the release of species of a biomass devolatilization process. The data includes release rates of N-compounds \( \text{NH}_3, \text{HCN} \) and \( \text{HCNO} \) (cf. Fig. 6.7) that can be used for the prediction of \( \text{NO}_x \) emissions.

The heating rates used in the experiments of de Jong et al. should be compared to values for \( \mathcal{H} \) observed in reverse combustion experiments. These heating rates can be estimated from measurements with thermocouples that are placed in the fuel layer during a reverse combustion experiment (cf. Fig. 6.4.2). The heating rate can be estimated by

\[
\mathcal{H} = \frac{T(t_{90\%}) - T(t_0)}{t_{90\%} - t_0},
\]

where \( t_{90\%} \) is defined as the time at which the temperature reaches 90% of its maximum value and \( t_0 \) is the time for which \( T = 400 \text{ K} \). This results in heating rates of \( \mathcal{H} = 162 \text{ K min}^{-1}, 729 \text{ K min}^{-1} \) and \( 370 \text{ K min}^{-1} \) for profiles \( T(t) \) obtained at \( m_{gu} = 1.25 \times 10^{-2}, 3.33 \times 10^{-2} \) and \( 5.78 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1} \), i.e. at values of the air flow close to zero, close to the maximum value of \( m_{gu} \) and close to extinction (cf. Fig. 5.4). Thus, for low values of \( m_{gu} \), the value of \( \mathcal{H} \) observed in the reverse combustion experiments approaches the maximum value of \( \mathcal{H} \) used in the experiments.

Because the release rate data is obtained from experiments, it contains fluctuations as a result of instabilities in the conversion process and imperfections in the measurement method. These fluctuations are strongest in the measurements of the less abundant species like the N-compounds (cf. Fig. 6.7). A method to deal with the fluctuations in the measurement data is described in the next section.

The measurements of the release rates are also affected by the time resolution of the FTIR measurement method. For higher heating rates, the conversion process is faster which results in less accurate measurements (cf. [72]). With respect to the time resolution, a compromise between data obtained at high heating rates and data with a sufficient time resolution was made by using the data obtained at \( \mathcal{H} = 25 \text{ K min}^{-1} \).

A large fraction of the mass loss is caused by the release of tars. This is a group of molecules whose properties are largely unknown, which makes it more difficult to take them into account in the LT. A general definition of tars does not exist. Often, the components with a boiling point above a certain temperature, for example \( T = 353 \text{ K} \), or the condensed fraction of the pyrolysis products are used as a criterion to identify the tars [46]. In the measurements of De Jong et al, the tar species are
Figure 6.4: Temperature profiles measured during fixed bed combustion experiments with a linear approximation of the gradient. Profiles obtained with uninsulated glass tube (cf. Chap 3) at air flows of \( m_{gu} = 1.25 \times 10^{-2}, 3.33 \times 10^{-2} \) and \( 5.78 \times 10^{-2} \text{ g cm}^{-2} \text{s}^{-1} \).

implicitly defined as the species released during devolatalization that are not identified with the FTIR measurements. In practice, this results in a group of species that is not very different from the species identified by the other criteria and therefore it forms the basis of the definition used here, namely the group of species for which (1) no release rates and (2) no kinetic data in the detailed kinetic mechanism for the gas phase is available. Currently, it is chosen not to take the tars into account in the LT because a detailed description is not available.

**Processing of TGA-FTIR measurement data**

To be able to use the data set in a numerical code, additional data processing was applied. The data processing involves two steps: (1) specification of the temperature range in which measurement data is used to obtain a well defined LT and (2) applying a moving average method to reducing the noise in the measured release rates.

First, the temperature range represented in the LT was specified by cutting of the TGA-FTIR measurement data between starting temperature \( T_s = 298 \text{ K} \) and final temperature \( T_f = 1173 \text{ K} \), corresponding to \( t_s = 0 \text{ min} \) and \( t_e = 27 \text{ min} \), respectively. (These numbers were obtained directly from the measurement data and imply a corrected heating rate of \( 32 \text{ K s}^{-1} \).) Outside this temperature range, source terms due to devolatalization are assumed to be zero.

Secondly, a moving average was applied to all release rate measurements to reduce the fluctuations in the results for \( \omega^{gs}_{i} \). The moving average filter that was used is given by

\[
< \omega^{gs}_{i} > (t_i) = \frac{1}{2\Delta t} \sum_{t_j} \omega^{gs}_{i}(t_j), \quad t_i - \Delta t \leq t_j \leq t_i + \Delta t \quad (6.34)
\]

where the brackets indicate an averaged value. Applying a moving average leads to a slight deformation of the profiles of the species source terms. The profiles of \( \omega^{gs}_{i} \)
Table 6.1: Yields of tar, char and gas for three experiments with wood pellets at different heating rates. Yields are expressed in weight percent of the original biomass on a dry and ash-free basis. Data from de Jong et al. [72].

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K · min⁻¹)</td>
<td>10</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Char</td>
<td>13.8</td>
<td>13.8</td>
<td>13.8</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>86.2</td>
<td>86.2</td>
<td>86.2</td>
</tr>
<tr>
<td>Tar</td>
<td>37.2</td>
<td>38.8</td>
<td>48.4</td>
</tr>
<tr>
<td>Gas</td>
<td>49.0</td>
<td>47.4</td>
<td>37.6</td>
</tr>
</tbody>
</table>

Figure 6.5: Data from TGA-FTIR measurements obtained by De Jong et al. [72]. Left: $\frac{m}{m_0}$: solid line, $T$: dashed line (TGA-data). Right: $Y_{\text{CH}_4}$ (example of FTIR data).

are scaled with a factor

$$f_{i_g} = \frac{\int_0^{t_e} \omega_{i_g} \, dt}{\int_0^{t_e} < \omega_{i_g} > \, dt}$$  \hspace{1cm} (6.35)

to correct for the deformation of the spatial profiles due to applying a moving average. Here, also a width of $\Delta t = 1 \text{ min}$ is used. To avoid unnecessary complex notation, the brackets for the average source terms $< \omega_{i_g} >$ are left out in the remainder of this chapter. Results of the application of the moving average method can be found in Fig. 6.6. The results show a significant reduction in the fluctuations while the general features of the profile have remained in tact.

6.4.3 Implementation

For the simulations with biomass, the same set of equations are solved as for coal. The set consists of solid phase equations given by Eqs. (6.1) and (6.3) of gas phase equations given by (6.6)-(6.9). The reaction mechanism GRI mech3.0 was used in the computations to describe the gas phase chemistry. A lookup table based on processed TGA-FTIR data for $\omega^{gs, D}(T_s)$ obtained at $\mathcal{H} = 25 \text{ K min}^{-1}$ was used to describe the devolatilization process. The char conversion was described with source terms $\omega^{gs, D i_g}(T_s)$ based on the explicit expression in Eq. (6.16). Only species present
Table 6.2: End yield of species determined from a TGA-FTIR experiment with wood-pellets at a heating rate of $30 \text{K} \cdot \text{min}^{-1}$. Indicated are also the species that are represented in the GRI-mech 3.0 mechanism. Data from de Jong [72].

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Total Yield</th>
<th>Present in GRI-mech 3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$\text{H}_2\text{O}$</td>
<td>16.0</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>$\text{CH}_3\text{CHO}$</td>
<td>8.11</td>
<td>Yes</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>6.77</td>
<td>Yes</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>$\text{CO}_2$</td>
<td>5.08</td>
<td>Yes</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>$\text{CH}_2\text{O}$</td>
<td>2.93</td>
<td>No</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$\text{CH}_3\text{COOH}$</td>
<td>2.37</td>
<td>No</td>
</tr>
<tr>
<td>Acetone</td>
<td>$\text{CH}_3\text{OCH}_3$</td>
<td>2.15</td>
<td>No</td>
</tr>
<tr>
<td>Formic acid</td>
<td>$\text{HCOOH}$</td>
<td>1.73</td>
<td>No</td>
</tr>
<tr>
<td>Methane</td>
<td>$\text{CH}_4$</td>
<td>1.30</td>
<td>Yes</td>
</tr>
<tr>
<td>Methanol</td>
<td>$\text{CH}_3\text{OH}$</td>
<td>0.74</td>
<td>Yes</td>
</tr>
<tr>
<td>Phenol</td>
<td>$\text{C}_6\text{H}_5\text{OH}$</td>
<td>0.65</td>
<td>No</td>
</tr>
<tr>
<td>Ethylene</td>
<td>$\text{C}_2\text{H}_4$</td>
<td>0.23</td>
<td>Yes</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>$\text{SO}_2$</td>
<td>0.12</td>
<td>No</td>
</tr>
<tr>
<td>Carbonyl sulphide</td>
<td>COS</td>
<td>0.11</td>
<td>No</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>HCN</td>
<td>0.09</td>
<td>Yes</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$\text{NH}_3$</td>
<td>0.02</td>
<td>Yes</td>
</tr>
<tr>
<td>Isocyanic acid</td>
<td>HNCO</td>
<td>0.02</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Figure 6.6: Processing of the data for the manifold: release rate of $\text{CH}_4$ (solid line) after processing of the original data (dashed line).
Figure 6.7: Release of N-precursors NH$_3$, HCN and HNCO. Dashed lines: original measurement data [72]. Solid lines: measurement data after applying a moving average.

Figure 6.8: Examples of species in the manifold: methane release as a function of $T$. 
in this mechanism as well as in the data for the heterogenous source terms were used in the computations.

For the enthalpy equation, the enthalpy of the solid phase \( h_s \) needs to be specified. This involves specification of \( c_{ps} \) and \( h_s^0 \). For \( c_{ps} \), a constant value is assumed. Then, the original expression for \( h_s \) given by Eq. 6.5 reduces to

\[
 h_s = c_{ps}(T - T_{ref}) + h_s^0.
\]  

(6.36)

For \( h_s^0 \), also a constant value is assumed, i.e.

\[
 h_s^0 = h_{s0}^0
\]  

(6.37)

This assumption is less appropriate for biomass because it undergoes stronger changes in its chemical and physical structure during the devolatalization process. It is used as a first approximation in the present calculations.

The further implementation of the model is similar as for coal. Because then there is only a single solid phase species, the equations for \( Y_{i_s} \) do not need to be solved. Only in the release rates of species the different processes of devolatalization and char conversion are noticeable. The implementation of equations in the reactive flow solver Chem1D [98] and the use of an interpolation routine is similar as for the computations with coal (cf. Sec. 6.3.3).

### 6.4.4 Results

In this section, results are presented for the manifold based on TGA-FTIR data. In Fig. 6.9 spatial flame profiles based on calculations with the manifold are presented. The results consist of spatial profiles for the porosity, temperatures, gaseous reactants and products and nitrogen compounds.

The division of the conversion in a devolatalization process and a char burnout process can be recognized in the results for the porosity. The curve for \( \epsilon \) (Fig. 6.9a) shows that due to the devolatalization step, \( \epsilon \) initially increases from \( \epsilon_u \) to \( \epsilon \sim 0.65 \). The combustion of the remaining char then causes a second increase of the porosity to \( \epsilon \sim 0.67 \).

The temperature profiles (Fig. 6.9a) show that the temperature of the solid phase near the unburnt side of the reaction zone increases due to the heat release of the pyrolysis process. Due to the heat transfer limitations, the temperature of the gas phase lags behind in this region. At around \( T = 800 \text{ K} \), \( T_g \) becomes larger than \( T_s \). Here, the temperature is sufficiently high to initiate combustion of the volatiles. The temperature \( T_s \) lags behind because the main heat release now takes place in the gas phase. At the end of the reaction zone, \( T_s \to T_g \) due to the heat exchange between the two phases.

The concentrations of the main gas phase species (Fig. 6.9b) are in agreement with the curves for the temperatures. The initial decrease of \( Y_{O_2} \) is due to the release of species into the gas phase, as it coincides with the initial increase of \( T_s \). However, the decrease is not due to gas phase combustion, because ignition of the gas phase mixture has not taken place yet. Instead, it is caused by the increase of \( m_g \) (Fig. 6.9c). The increased value of \( m_g \) together with the constant value of \( m_{O_2} \) results in
6.5 Modeling an element of biomass

A complete description of the source term in the reverse combustion model requires the tar mass release $\omega_{gs,D}^{T}$, the elemental composition $Z_{Tie}$ and the enthalpy of formation of the solid $h_{s}^{0}$ during the conversion process. Here, it is shown how closure of the mass balance, elemental balance and enthalpy balance can be used to obtain expressions for $\omega_{gs,D}^{T}$, $Z_{Tie}$ and $h_{s}^{0}$ (Sec. 6.5.1). With the theoretically derived results, $\omega_{Tie}^{gs,D}$ and $Z_{Tie}$ are calculated for the TGA-FTIR data and on the basis of $Z_{Tie}$ an effective tar conversion reaction is written down (Sec. 6.5.2). Calculation of $h_{s}^{0}$ from measurement data falls outside the scope of this chapter.

a decreasing $Y_{O_2}$. The sharp decrease that follows is caused by the ignition of the volatiles. The sharp decrease then changes into a more gradual decrease, related to the char burnout reaction that is also responsible for the gradual increase of the porosity towards the end of the reaction zone.

The release of intermediate species (Fig. 6.9c) coincides with the initial increase of $T_s$. It can be seen that the acetaldehyde ($\text{CH}_3\text{CHO}$) is rapidly converted into products, as its concentration decreases rapidly towards the end of the reaction zone. A small amount of CO is left at the burnt side of the reaction zone.

The spatial profiles of N-compounds are presented in Fig. 1.4. It can be seen that the N-precursors are released at the downstream part of the reaction zone. When the flame is ignited and the gas phase chemistry starts, all precursors are oxidized to NO. Because the model does not yet include reactions for char gasification, the CO$_2$ formed during combustion is not used for char gasification. This means that the gas mixture resulting from the combustion process is exactly stoichiometric. For the process of reburning the NO to HCN and NH$_3$, fuel rich conditions are required. Therefore, this process does not take place in the current model results. It should be noted that this is not a fundamental problem as it can be solved by extending the set of heterogenous reactions.

The velocity $m_{su} = 0.32 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$ observed for $m_{su} = 2.8 \times 10^{-2} \text{ g cm}^{-2}\text{s}^{-1}$ observed in these calculations is not in agreement with the values for coal nor wood. The disagreement of the actual value of the velocity can be attributed to two causes: the data used for the calculations and the constant value chosen for the enthalpy of formation of the solid. The data used for the model is currently based on both coke and biomass: all the material properties (e.g. density, specific heat) are for coke, while the reaction source term is based on biomass devolatilization. Another cause is the data used for the manifold. The heating rate observed in fixed bed experiments can be an order of magnitude higher than the heating rate applied in the TGA-FTIR experiments used to generate the manifold. Finally, a large part of the mass release is currently not taken into account in the model because no gas phase equation for the tars has been implemented. The constant value of the enthalpy of formation in Eq. 6.37 may also cause problems.
Figure 6.9: Spatial flame profiles of $T_s$, $T_g$ and $\epsilon$ (a), mass fractions of main combustion reactants and products (b), mass fractions of intermediate species (c) and mass fractions of N-compounds (d).
6.5 Modeling an element of biomass

6.5.1 Theory

From a mass balance, the tar mass release $\omega^gs_T$ can be calculated. This mass balance reads:

$$\omega^gs_T(t) = \omega^gs_M - \sum_{i_g=1}^{N} \omega^gs_{i_g}(t).$$  \hfill (6.38)

It states that the tar mass release is equal to the total mass release of the solid fuel $\omega^gs_M$ converted into volatiles minus the contribution of the $N$ gas phase species $i_g$. In an equation, this reads In writing down this equation it is assumed that only the species present in both the gas phase kinetic mechanism and in the TGA-FTIR data are represented by the $i_g$.

The average elemental composition of the tars can be determined by writing down an elemental balance for the the element $Z_{ie}$ during the conversion process:

$$Z_{M,ie} \omega^gs_M = \sum_{i_g=1}^{N} Z_{i_gie} \omega^gs_{i_g} + Z_{T,ie}(t) \omega^gs_T,$$  \hfill (6.39)

where $\omega^gs_M$ indicates the total mass source term and $Z_{M,ie}$ the mass fraction of element $i_e$ in the total mass release $M$. This equation can be integrated from from $t = 0$ to $t = \infty$. This results in

$$Z_{T,ie} = \frac{\rho_s(0) (Z_{sie}(\infty) - Z_{sie}(0)) - \int_{t=0}^{\infty} \sum_{i_g=1}^{N} Z_{i_gie} \omega^gs_{i_g} \, dt}{\int_{t=0}^{\infty} \omega^gs_T \, dt},$$  \hfill (6.40)

if it is assumed that the elemental composition of the tars $Z_{T,ie}$ is constant during the experiment and that release of the element $i_e$ during conversion $\int_{0}^{\infty} Z_{M,ie} \omega^gs_M \, dt$ is equal to the change in the mass of the element in the solid phase, given by $Z_{sie}(\infty) - Z_{sie}(0)$.

An expression for $h_{s0}$ can be obtained by writing down the enthalpy balance of an isothermally devolatalizing biomass particle:

$$\frac{d (\rho_s h_s)}{dt} = \sum_{i_g=1}^{N} \omega^gs_{i_g} h_{i_g} + \omega^gs_T h_T + \frac{Q}{\rho_s}$$  \hfill (6.41)

Here, $Q$ is a source term for the heat supplied for the devolatalization process. Integrating the enthalpy balance leads to

$$\rho_s(t) h_s(t) - \rho_s(0) h_s(0) = \int_{0}^{t} \sum_{i_g=1}^{N} \omega^gs_{i_g} h_{i_g} \, dt + \int_{0}^{t} \omega^gs_T h_T \, dt + \int_{0}^{t} Q \, dt$$  \hfill (6.42)

The enthalpy of the solid can be written down explicitly, resulting in

$$h^0_s(t) = \rho_s(t)^{-1} \int_{0}^{t} \left( \sum_{i_g} \omega^gs_{i_g} h_{i_g} + \omega^gs_T h_T + \frac{Q}{\rho_s(0)} \right) \, dt + \frac{\rho_s h^0_s(0)}{\rho_s(t)} - c_{ps} (T(t) - T_{ref})$$  \hfill (6.43)
Here, the density $\rho_s$ can be determined on the basis of the mass balance, $h_{0s}^0$ can be determined on the basis of the heat of combustion (cf. Sec. 6.3.1), $c_{ps}$ can be assumed constant, $\omega_i g$ can be obtained from the TGA-FTIR data, $h_{ig}$ can be obtained from data from the literature (as done for the reverse combustion modeling) and $\omega_i g^s$ has been derived in this section. Thus, only the parameters $h_{0s}^0$ and $Q$ are unknown. For $h_{0s}^0$, data from a heavy hydrocarbon species from the literature could be used (e.g. benzene). The determination of $Q(t)$ could be performed with a DSC (Differential Scanning Calorimeter)(cf. e.g. [121]). Then, $h_{0s}^0(t)$ can be determined from the experiments.

Summarizing, the results presented here indicate that the lookup table has to be extended with two data rows, i.e. $\omega_i g^s(\chi_i)$ and $h_{0s}^0(\chi_i)$. The tar elemental composition $Z_{Ti}_g$ does not need to be taken into account in the LT because it is constant.

### 6.5.2 Application: tar mass release and elemental composition

The TGA-FTIR data set was used to determine the tar mass release term $\omega_i g^s$ and the tar elemental composition $Z_{Ti}_g$. To perform this task, first the measurement data are processed further to determine the total mass release from the TGA-FTIR results and to correct minor deviations in the measurement data due to measurement errors. Then, $Z_{Ti}_g$ is determined. Finally, a single step reaction is proposed for the conversion of the tars.

The mass release $\omega_i g^s_M$ was determined from the curve for $M(t)/M_0$ by means of a moving fit method. For each measurement at time $t_i$ a linear fit was made in the profile $M(t)$ in the region $[t_i - \Delta t, t_i + \Delta t]$. The slope of the fitted line was used as the value for the mass source term. The range for the moving fit used was $\Delta t = 1$ min. This value was chosen because it is small enough to leave the shape of the curve in tact, while it is large enough to prevent fluctuations in the derived source term arising due to the discrete nature of measurements of the mass.

The tar release $\omega_i g^s_T$ was determined by applying Eq. 6.38, substituting the calculated mass loss source term $\omega_i g^s_M$ and the species release rates $\omega_i g^s$. The $N$ species $i_g$ are species that are present in both the kinetic mechanism GRI-mech30 and in the TGA-FTIR data. Because this group of species is smaller than original number of species in the TGA-FTIR data, the total gas yield decreases from 43.9% to 33.9% of the original mass of the solid.

The resulting source term $\omega_i g^s_M$ of applying the moving fit method to the profile $m(t)$ is presented in Fig. 6.10.

Computations of $\omega_i g^s_T(t)$ showed that there were time intervals where $\omega_i g^s_M$ was smaller than the mass loss $\sum_{i_g=1}^N \omega_i g^s(t)$. This resulted in small negative values for $\omega_i g^s_T(t)$ in these time intervals (cf. Eq. 6.38). This was corrected by subtracting the excess mass loss from the species release rates, starting with the most abundant species $CO_2$, followed by $CO$, $H_2O$, and $CH_4$ respectively, until the source term $\omega_i g^s_T(t)$ became zero in these regions. The corrections resulted a further, small decrease of the total gas yield from 33.9% to 32.5%. The result for $\omega_i g^s_T$ can be found in Fig. 6.10.

In order to calculate $Z_{Ti_e}_g$, Eq. (6.40) is used. In this expression, $\omega_i g^s_T(t)$ is substituted together with the elemental composition $Z_{i_g}_e$ and the release rates $\omega_i e$ of the gas phase species. For $Z_{i_e}(0)$, the initial elemental composition given in Ref. [72] was
6.6 Conclusions

In this chapter, a biomass combustion model with detailed chemistry has been described. The model is based on a set of transport equations for the gas phase and the solid phase with a lookup table for the reaction source term. The model was tested first with a lookup table to describe coal conversion. After this, a lookup table with detailed species release rates obtained from TGA-FTIR data and a detailed kinetic gas phase mechanism (GRImech3.0) that includes reactions for nitrogen compounds was used to describe biomass conversion.

The results for coke can be considered as a test for the model. It is shown that the model implementation results in mass and enthalpy conservation. This indicates that the model framework is in order. Furthermore, the results show that the model can describe the behavior of the temperature and velocity as a function of air mass flow experiments and is able to predict the spatial profiles of species in the reaction zone.

The results for the conversion of biomass show that by including a lookup table with TGA-FTIR release rate data and detailed gas phase chemistry it is possible used while for $Z_i(\infty)$ it is assumed that at the end of the TGA-FTIR experiment all solid material consisted of carbon only. Then, an overall elemental tar composition $C_{Z_C}H_{Z_H}O_{Z_O} = CH_{1.07}O_{0.56}$ is obtained.

In the reaction mechanism, an assumption has to be made for the combustion of tar species. First, it was attempted to reduce the tar to larger hydrocarbon species present in the gas phase kinetic mechanism GRImech3.0 because this resembles closest the actual chemistry. The minimum number of species that is required to match all values for $Z_H$, $Z_O$ for a given $Z_C$ is two. However, the derived tar composition has a low value for $Z_H$ compared other species in the GRImech3.0 mechanism, for example, methane $Z_H = 3$ and propane ($Z_H = 2.67$). Therefore, the second option has to be followed: a similar to the reaction presented in Eq. 6.19 can be added to the gas phase mechanism with a rate expression derived from expressions for single step reactions for other species, e.g. methane.
to describe the first stage of NO\textsubscript{x} formation in a grate furnace. The observation
that the released N-precursors are all oxidized to NO is caused by the non-fuel rich
conditions of the gas phase downstream of the reaction zone, which is in turn a
result form the simplified heterogenous reaction process of char. The gas and solid
temperatures show a considerable increase during the devolatalization phase, for
which the reason is not yet known. This might be caused by assuming the enthalpy
of formation of the solid constant during the conversion process.

The lookup table approach was shown to provide an efficient description of the
reaction source term for an element of biomass in the reverse combustion model. In
addition, a further outline of possible extensions of the lookup table approach were
proposed (although they were not applied in the reverse combustion model). It was
shown how closure of the mass balance, elemental balance can be used to calculate
the tar mass release rate and elemental composition as well as the enthalpy of
formation of the solid during the conversion process. The resulting equations were
applied to the TGA-FTIR, resulting in the tar mass release rate and the elemental
composition. Based on the elemental composition, it was proposed to add a single
step reaction for the tar conversion in the reverse combustion model. Because the
TGA-FTIR data does not contain information about the energy balance, the solid
enthalpy of formation was not determined.

For future research on the reverse combustion model it is recommended to solve
the observed deviations in the temperature profile. Then, it would be suitable to use
the model with an extended set of data to describe the physical and chemical con-
version process more accurately (e.g. additional heterogeneous reactions for char
gasification, a detailed kinetic mechanism for biogas kinetics and an extended ver-
sion of the lookup table).

The lookup table approach can be used as a framework to increase experimen-
tal knowledge of the conversion process, for example for a further identification
of tar species, an investigation of the enthalpy balance or measurements at higher
heating rates. Such an extended lookup table represents the conversion of a single,
isothermal element of biomass, which can be used as a fundamental unit for vari-
ous biomass conversion processes (e.g. fluidized beds, pulverized fuel combustion,
single particle conversion).
Chapter 7

Conclusions

In this thesis, a numerical model for reverse combustion with detailed chemistry has been developed. An existing, basic 1-D model consisting of three transport equations for solid, gas and energy has been used as a foundation for this model. First, it has been investigated if the basic model can be used to describe the reverse combustion process accurately (Chap. 4). This investigation focuses on the effect of heat and mass transport to single fuel particles in the fuel layer on the structure of the conversion front. Subsequently, it has been studied numerically and experimentally how heat losses due to an imperfectly designed fixed bed reactor can result in deviations of the measured front velocity, thus impairing model validation (Chap. 5). Finally, the 1-D model has been extended with a detailed description of the chemical processes occurring in the reaction zone during the conversion process to be able to use the model for NO\textsubscript{x} predictions (Chap. 6).

The investigation of the effects of heat and mass transfer on the structure of the reaction front shows that two limiting front structures exist. In the kinetically controlled limit, the conversion front consists of a distinct preheat zone and reaction zone with the maximum value of the reaction source term located at the burnt side of the conversion front. In the mass transfer controlled limit, the maximum value of source term is located near the unburnt side of the reaction front, while a separate preheat zone and reaction zone are not observed. The numerical solutions were compared to analytical solutions of the model equations. The analytical results were found to be correct only in the kinetically controlled limit. This result leads to the conclusion that numerical methods should be used for reasons of accuracy, even in case the model solutions are required to be used for computationally intensive purposes like algorithms for process control of a grate furnace.

The study of the effect of heat losses in reverse fixed bed combustion experiments due to imperfect reactor design has been focused on three heat loss mechanisms: heat loss (1) to the environment due to imperfect insulation of the reactor, (2) to the reactor walls due to instationary heating and (3) to the unburnt fuel by means of heat conduction by the walls (preheating effect). Based on a comparison of 1-D and 2-D model results, it was concluded that heat losses should be reduced in the experimental setup instead of taking them into account into a 1-D model. An experimental and numerical parameter study was performed aimed at investigating how the heat loss effects can be minimized experimentally. This study showed that
Conclusions

even for a perfectly insulated reactor, heat loss mechanisms (1) and (3) can lead to deviations in the conversion front velocity of $O(10\%)$. Furthermore, it is shown that using a large reactor diameter and a material with a low density, specific heat and thermal conductivity can be used to reduce these deviations. More specific, ceramics could be used as a wall material. It is recommended to use the 2-D model to develop an improved fixed bed reactor for future 1-D model validation.

The development of a reverse combustion model with detailed chemistry illustrates that it is possible to describe the release rates of species from the solid fuel. A new approach was followed for this: a lookup table on the basis of experimental data was used, in which the release rates were stored as a function of the temperature. The results show that the release and evolution of nitrogen compounds, processes that play an essential role in the formation of NO$_x$ in a grate furnace, can be described with such a model. A topic for further improvement for the model is formed by the strong increase of the temperature related to the devolatalization process. In the future, three main improvements can be made to the model: (1) the physical and chemical processes in the model can be improved (e.g. by including radiation and additional char gasification reactions); (2) the lookup table can be extended to account for the release of tars changes in the solid enthalpy; (3) the approach of using a lookup table can be extended by including data obtained under a wider range of experimental conditions that resemble reverse combustion conditions more closely. For the latter, the number of progress variables in the table can be extended with, for example, the heating rate.

The results in this thesis have several broader scientific, technical and social implications. Two major scientific implications can be identified. Firstly, the lookup table approach provides a framework for the development of a coherent data set for the conversion of a single unit of biomass involving both mass release, species release and enthalpy release. Such a data set can be used for a broad range of biomass conversion processes (pyrolysis, gasification, combustion) and reactors (grate furnace, fluidized bed, pulverized fuel combustor). Secondly, the deviations observed in the experimental determination of the conversion front imply that future fixed bed reactors have to be designed more carefully to obtain accurate front velocity measurements for model validation.

An important technical implication is that a detailed fixed bed model is now available that can be used in an overall CFD model for grate furnace conversion. This means that engineering companies can use the results of the fixed bed model to perform parameter studies with respect to furnace design and operating conditions to optimize the conversion process for NO$_x$ emissions and energy output.

Finally, an important social implication is that on the long term, optimized furnaces increase the attractiveness of biomass grate furnace conversion for companies and customers. Increased application of biomass conversion for energy production contributes to a diversification of our energy supply and a better environment.
Appendix A

The enthalpy equation for fixed bed combustion

In a model for fixed bed combustion, transport of energy can be described by means of equations in terms of the enthalpy of the solid phase (subscript \(s\)) and the gas phase (subscript \(g\)). The solid phase exchanges mass and heat with the gas phase. Due to heterogeneous reactions, enthalpy is exchanged between the phases. If it is assumed that the heterogeneous reactions release their heat to the solid, the transport of heat to the solid phase can be described with a heat transfer coefficient \(k\). The exchange of mass between the two phases will lead to an additional exchange term \(\phi\) in the enthalpy equation, because mass transport and enthalpy export are coupled. For this exchange term, an expression has to be obtained. This is done here by rewriting the equation for the enthalpy \(h\) in terms of the temperature. To avoid unnecessarily complex notation in this derivation, the convective and diffusive terms are assumed to be zero, although the derivation can be also be performed without this assumption. The enthalpy equations for the solid phase and the gas phase are:

\[
\frac{d}{dt} (\epsilon \rho_g h_g) = \phi + k (T_s - T_g) \quad \text{(A.1)}
\]

\[
\frac{d}{dt} ((1 - \epsilon) \rho_s h_s) = -\phi - k (T_s - T_g) \quad \text{(A.2)}
\]

where \(\rho\), \(T\) the temperature and \(\epsilon\) the porosity. For the gas phase, this can be written as

\[
\epsilon \rho_g \frac{dh_g}{dt} + h_g \frac{d(\epsilon \rho_g)}{dt} = \phi + k (T_s - T_g) .
\]

(A.3)

Three additional equations are required to formulate this equation in terms of the temperature. The first equation is the species conservation equation given by

\[
\frac{d (\epsilon \rho_g Y_{i_g})}{dt} = \omega_{i_g}^{gs} + \epsilon \omega_{i_g}^g .
\]

(A.4)

Here, \(Y\) is a species mass fraction, \(i_g\) an identifier that runs over all species within the gas phase and \(\omega\) a source term. The source terms for heterogeneous reactions are treated separately and are indicated with ‘\(gs\)’. Heterogenous reactions are defined
The enthalpy equation for fixed bed combustion as reactions in which reactions occur that involve species from both the gas and the solid phase. The second equation is the continuity equation for the gas phase,

\[
\frac{d (\epsilon \rho g)}{dt} = \sum_{i_g} \omega_{i_g}^{gs}. \tag{A.5}
\]

The third equation is the relationship between a gradient in the enthalpy, gradients in the mixture components and the temperature gradient, i.e.

\[
dh = \sum_i d (h_i Y_i) = \sum_i c_p dT + \sum_i h_i dY_i = c_p dT + \sum_i h_i dY_i, \tag{A.6}
\]

where \( c_p \) is the specific heat at constant pressure. Here, this expression can be used in the form

\[
\frac{d h_g}{dt} = \sum_{i_g} \left( h_{i_g} \frac{d Y_{i_g}}{dt} \right) + c_{pg} \frac{dT_g}{dt}. \tag{A.7}
\]

Substituting Eq. A.7 in Eq. A.3 and rearranging the result leads to

\[
\epsilon \rho g c_{pg} \frac{dT_g}{dt} = \phi - \sum_{i_g} \omega_{i_g}^{gs} \frac{d}{} - \sum_{i_g} h_{i_g} \frac{dY_{i_g}}{dt} + k (T_s - T_g). \tag{A.8}
\]

Using the definition of the enthalpy \( h = \sum_i Y_i h_i \) and substituting Eq. A.5 leads to

\[
\epsilon \rho g c_{pg} \frac{dT_g}{dt} = \phi - \sum_{i_g} h_{i_g} Y_{i_g} \sum_{j_g} \omega_{j_g}^{gs} - \epsilon \rho g \sum_{i_g} h_{i_g} \frac{dY_{i_g}}{dt} + k (T_s - T_g). \tag{A.9}
\]

In the third term on the rhs. of this equation, the expression

\[
\epsilon \rho g \frac{dY_{i_g}}{dt} = \frac{d (\epsilon \rho g Y_{i_g})}{dt} - Y_{i_g} \frac{d (\epsilon \rho g)}{dt} = \omega_{i_g}^{gs} + \epsilon \omega_{i_g}^{g} - Y_{i_g} \sum_{i_g} \omega_{i_g}^{gs} \tag{A.10}
\]

can be substituted. This leads to

\[
\epsilon \rho g c_{pg} \frac{dT_g}{dt} = \phi - \sum_{i_g} h_{i_g} \omega_{i_g}^{gs} - \sum_{i_g} h_{i_g} \epsilon \omega_{i_g}^{g} + k (T_s - T_g). \tag{A.11}
\]

The third term on the rhs. can be recognized as the heat release due to the homogeneous reactions. In the description of the fixed bed combustion process given here, the heat release by the heterogeneous reactions is assumed to take place in the gas phase only. This means that only this term is allowed to be left on the rhs. It follows that

\[
\phi = \sum_{i_g} h_{i_g} \omega_{i_g}^{gs} \tag{A.12}
\]

in order to obtain

\[
\epsilon \rho g c_{pg} \frac{dT_g}{dt} = - \sum_{i_g} h_{i_g} \epsilon \omega_{i_g}^{g} + k (T_s - T_g). \tag{A.13}
\]
For the solid phase reactions, the same procedure can be followed. This leads to an expression similar to Eq. A.11 for the solid phase:

\[
(1 - \varepsilon) \rho c_{ps} \frac{dT_s}{dt} = \phi - \sum_{i_s} h_{i_s} \omega_{gs} - \sum_{i_s} h_{i_s} (1 - \varepsilon) \omega_{is} - k (T_s - T_g). \tag{A.14}
\]

The expression for \( \phi \) (Eq. A.12) can be substituted in this equation, leading to

\[
(1 - \varepsilon) \rho c_{pg} \frac{dT_s}{dt} = - \sum_{\eta=i_s,i_g} h_{\eta} \omega_{\eta}^{gs} - \sum_{i_s} h_{i_s} (1 - \varepsilon) \omega_{is} - k (T_s - T_g). \tag{A.15}
\]

Here, the first term on the right hand side represents the heat generated by the heterogeneous reactions, which was required to be released in the solid phase. This means that the enthalpy equations for the gas and the solid phase (Eqs. A.1, A.2) can now be written as

\[
\frac{d (\varepsilon \rho h_g)}{dt} = \sum_{i_g} h_{i_g} \omega_{i_g}^{het} + k (T_s - T_g) \tag{A.16}
\]

\[
\frac{d ((1 - \varepsilon) \rho h_s)}{dt} = - \sum_{i_g} h_{i_g} \omega_{i_g}^{het} - k (T_s - T_g) \tag{A.17}
\]

Assuming that the heat exchange between the two phases is fast (i.e. \( k \to \infty \)) results in \( T_s = T_g \). Adding the two equations then results in

\[
\frac{d (\rho h)}{dt} = 0 \tag{A.18}
\]

with \( \rho h = \varepsilon \rho h_g + (1 - \varepsilon) \rho h_s \). This equation expresses the overall conservation of enthalpy. Summarizing, the resulting equations for the enthalpy (Eqs. A.16 and A.17) give a complete and consistent description of energy conservation in a gas-solid system with heterogeneous reactions.
The enthalpy equation for fixed bed combustion
Appendix B

Temperature and solid velocity at the extinction point

In this appendix, it is shown how for the values $T_b$ and $m_{su}$ at the extinction point general expressions can be derived that can be used to calculate the lines indicated with $S$ in Fig. 4.4. The expressions can be derived by the integral balances over the domain for the species and the temperatures, which are obtained by integrating the stationary set of equations (Eq. 4.13, 4.14 and 4.15) over the domain. For the equation for the oxygen mass fraction, this results in

$$\int_{-\infty}^{\infty} \left(v_s \frac{d}{dx} (\epsilon \rho_g Y) + \frac{d}{dx} (\epsilon \rho_g v_g Y) - \frac{d}{dx} \left(\rho_g \frac{dY}{dx}\right)\right) dx = -\int_{-\infty}^{\infty} \omega R dx,$$  \hspace{1cm} (B.1)

which can be expressed as

$$[v_s \epsilon \rho_g Y + v_g \epsilon \rho_g Y]_u^b = -\int_{-\infty}^{\infty} \omega R dx.$$  \hspace{1cm} (B.2)

Integrating the equation for the porosity, Eq. 4.13 leads to

$$[v_s (1 - \epsilon \rho_s)]_u^b = -\int_{-\infty}^{\infty} \omega R dx.$$  \hspace{1cm} (B.3)

Combining equations B.2 and B.3 and substituting $Y_b = 0$, and $\epsilon_b = 1$, which is generally the case at the extinction point, leads to an expression for the solid velocity at the extinction point:

$$v_{s,S} = \left(\frac{\omega (1 - \epsilon_u) \rho_s}{Y_u \epsilon_u \rho_{gu}} - 1\right)^{-1} v_{gu,S}.$$  \hspace{1cm} (B.4)

Assuming that the parameter $p = \frac{\omega (1 - \epsilon_u) \rho_s}{Y_u \epsilon_u \rho_{gu}} \gg 1$ and using the expressions for the mass flows given by Eq. 4.4 and 4.18 results in

$$m_{su,S} = \frac{Y_u}{\omega} m_{gu,S},$$  \hspace{1cm} (B.5)

which is equivalent to Eq. 4.36 For the temperature, a similar procedure can be followed. However, instead of using Eq. 4.15 for this procedure, it is more convenient
to use Eq. 4.40 while neglecting the term with indicated with a star by assuming $v_s \ll v_g$, which is the case when $p \gg 1$. Then, integrating and substituting expressions for the mass flows lead to

$$m_{su} \left( \frac{1 - \epsilon_u}{1 - \epsilon_b} \right) c_{ps} T_b - m_{su} c_{ps} T_u + m_{gb} c_{pg} T_b - m_{gu} c_{ps} T_u = -\int_{-\infty}^{\infty} \Delta H_r Rdx. \quad (B.6)$$

Combining this equation with Eq. B.2, using $m_{gu} = m_{gb}$ and substituting $Y_b = 0$ and $\epsilon_b = 1$ as well as relation B.5 leads to the expression

$$T_{b,S} = T_u \left( \frac{Y_u c_{ps}}{\omega c_{pg}} + 1 \right) - \frac{Y_u \Delta H_r}{\omega c_{pg}}, \quad (B.7)$$

which is equivalent to Eq. 4.37. For the data presented in table 4.1, $p = 7 \times 10^3$, justifying the assumption $p \gg 1$. 
Bibliography


Summary

Grate Furnace Combustion: A Model for the Solid Fuel Layer

The use of numerical models in the design process of biomass fired grate furnaces can help to reduce NOx emissions and to make the combustion process more efficient. This thesis focuses on the development of a model for the solid fuel layer that can serve as part of an overall CFD (Computational Fluid Dynamics) model of the complete furnace. The model can describe the chemistry in the solid fuel layer in detail, including the nitrogen compounds. An experimental setup is developed aimed at model validation.

The 1-D numerical model that has been developed describes the reverse combustion of the fuel layer, i.e. the propagation of a reaction front through a porous fuel layer of fuel particles in the opposed direction of the air flow. An existing, basic 1-D numerical model (Gort, 1995) was used as a foundation. The model was extended by including TGA-FTIR measurement data for the species release rates during devolatilization. The TGA-FTIR data is stored in a lookup table as a function of the solid temperature and is retrieved from the table by the model during the numerical simulations. The evolution of the released species in the gas phase in the void space of the fuel layer was performed by applying detailed gas phase kinetic mechanisms. The inclusion of detailed chemistry and the use of a lookup table are new in comparison with other reverse combustion models.

The experimental setup that has been constructed consists of a cylindrical fixed bed reactor in which a reverse combustion process can be studied by following the conversion front by means of thermocouples placed at fixed distances in the fuel layer and a mass balance on which the reactor is placed. The setup was designed such that the effect of heat losses to the reactor environment and to the reactor walls on the conversion process could be studied. The reactor wall can easily be changed from metal to quartz and if desired, an insulating layer can be attached to the setup. In other fixed bed experiments, a fixed reactor configuration was used which prohibits to investigate the effect of reactor design on the conversion process.

First results of numerical modeling were obtained on the basis of the set of equations. These results were used to investigate the effects of heat and mass transport limitations to and in the fuel particles on the structure of the reaction front. The numerical solutions show that two limiting front structures exist. In the kinetically controlled limit, the conversion front consist of a distinct preheat zone and reaction zone, while in the mass transfer controlled limit, such a distinction is not observed.
The numerical results were compared with existing analytical solutions, which has the advantage of a reduced computational effort. The analytical solutions were found to be correct in the kinetic limit only. It is therefore advised to use numerical solutions only, even when a low calculation time is important, e.g. in process control algorithms for a grate furnace.

Results obtained with the final model show that the release and evolution of various chemical species can be described with the implementation of detailed chemistry. In particular, the chemistry of nitrogen compounds can be modeled, which is a processes that plays an essential role in the formation of NO\textsubscript{x} in a grate furnace. The lookup table approach is shown to provide the opportunity to extend the model with the release and conversion of tar release and an improved description of the enthalpy of the solid phase during the conversion process.

The experimental study showed that imperfect reactor design results in the presence of three heat loss mechanisms that affect the conversion process: heat loss (1) to the environment due to imperfect insulation of the reactor, (2) to the reactor walls due to instationary heating and (3) to the unburnt fuel by means of heat conduction by the walls (preheating effect). Experimental results, supported by results of simulations with a 1-D and 2-D implementation of the basic model equations showed that even for a perfectly insulated reactor with a steel wall, heat loss mechanisms (1) and (3) can lead to deviations in the conversion front velocity of \mathcal{O}(10\%). A parameter study with the 2-D set of model equations showed that a large reactor diameter and a wall material with a low density, specific heat and thermal conductivity can be used to reduce these significantly. Ceramics could be used as material.

Overall, the results from the modeling work presented in this thesis show that the use of detailed chemistry by applying a lookup table in combination with elaborate gas phase kinetics is a suitable approach to describe pollutant formation.
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