Biomass Particle Ignition in Mill Equipment

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Biomass Particle Ignition in Mill Equipment
Lars Schwarzer
Preface

This thesis summarizes the outcome of research on “Biomass particle ignition in mill equipment”. The work was carried out at the Combustion and Harmful Emission Control research center (CHEC) at the Department of Chemical and Biochemical Engineering at the Technical University of Denmark (DTU). Additional experimental data were collected during a three months’ research visit to the Laboratory of Inorganic Chemistry at Åbo Akademi, Finland. Project funding by DTU, Energinet and Ørsted A/S are gratefully acknowledged. The PhD-studies were supervised by Senior Researcher Peter Arendt Jensen (DTU), Professor Peter Glarborg (DTU), Lead Process Chemistry Specialist Jens Kai Holm (Ørsted) and Professor Kim Dam-Johansen (DTU).

A word of thanks...

I’d like to say a few personal words of thanks at this point, to all who have supported and made this project possible. To Peter Arendt Jensen and Peter Glarborg, thank you for the many, sometimes intense, but always friendly and fruitful discussions! I’ve learned a lot from you, and this work would look a lot differently without. I would like to thank Kim Dam-Johansen for pointing me to interesting issues I would otherwise have overlooked, and Jens Kai Holm for adding an industrial perspective to this work.

Also at DTU, a big thanks to Zsuzsa Sárossy for carrying out the composition analysis for the biomasses – what started out as a vague idea turned out to be one of the major building blocks of this work. I’m very grateful to Stig Wedel for patiently explaining the intricacies of mathematical modelling, and helping me get some of my ideas sorted out. Thanks to Tareq Abdulrahman, a master student I co-supervised, for carrying out the initial set of TGA-measurements. Furthermore, I’d like to acknowledge Nikolaj Vinterberg Nissen, Anders Kjersgaard, Lars Møller and the KT workshop for keeping the measurement equipment running, and Lilian Beenfeldt Holgersen for generously extending my TGA bookings.
During my PhD studies, I had the opportunity to spend some time at the Laboratory of Inorganic Chemistry at Åbo Akademi in Turku, Finland. I’d like to thank Professor Leena Hupa and her group for the very kind welcome! Special thanks to Oskar Karlström for discussions about everything from science to philosophy, and to Luis Bezerra for letting me play around with the single particle reactor.

Working away on your PhD-project can feel a bit lonely at times – I’d like to thank my fellow PhD students for numerous times of sharing a joke, a drink or a game, and keeping up the social life. Things would definitely not have been the same without my two long-term office mates Kristian and Giovanni. It was always great to be able to vent an idea (and also the occasional frustration) – mostly, though, it was a shared dry, sometimes dark, sense of humor which made 125 a second home!

Finally, to my family, whose encouragement and moral support throughout the years have been invaluable: Mom, Dad, Grandma, Simone & Johannes – Danke!

Lars Schwarzer
June 2019
Summary

In the last decades, interest in replacing fossil fuels with renewable energy sources has increased, largely motivated by environmental concerns. One alternative to coal and gas is biomass, especially for combined heat and power production. Biomass can play an important role in an all-renewable energy scenario: unlike solar or wind power, it can easily be stored in large quantities and converted when demand for heat and electricity arise. Power plants designed for pulverized coal firing have successfully been converted to biomass (especially wood) dust firing. Use of biomass dusts to replace pulverized coal in combined heat and power plants has however led to several incidents in which fires broke out in the plants’ mills. Mill fires are likely caused by self-heating and spontaneous ignition of settled dust accumulations. Transport air passing through the mills is pre-heated, which serves to both dry the fuel and also as a method of internal heat recovery in the power plant. High combustion air temperatures are therefore desirable from the point of view of overall plant efficiency, but poor predictability of critical conditions for mill fires has led operators to adopt cautiously low inlet air temperatures ($\leq 423$ K).

In this work, results from a study on single pellets (0.25 g) suggested that heterogeneous oxidation of biomass is the main mechanism leading to mill fires. Small wood pellets spontaneously ignited when exposed to temperatures around 500 K and above. Ignition led to large temperature increase of the sample, emission of significant amounts of CO and CO$_2$ and near-complete conversion of the organic matter. Ignition occurring at low temperatures was distinct from flaming modes of combustion. Flaming required higher ambient temperatures (>700 K). From a carbon balance, it was concluded that a pyrolytic decomposition occurs in parallel to the oxidation. Both processes likely occur at rates in similar order of magnitude.

A simple reaction mechanism was developed to describe parallel oxidation and pyrolysis of biomass at low temperatures. The mechanism takes the composition of biomass into account, distinguishing between volatilizable fractions of extractives, hemicellulose, lignin and cellulose, as well as char. Analytical data was available for six biomasses: beech and pine wood, wheat straw, sunflower husk pellets, and two types of commercial wood pellets. Kinetic parameters were fitted to data measured in stepwise-isothermal ther-
mogravimetric analysis at 423–523 K. The models were in good agreement with the experimental data, and could to some degree also be extrapolated to higher heating rates (5 K/min) and temperatures (ca. 550–650 K). It was found that low temperature pyrolysis required a four-species model (extractives, hemicellulose, lignin, cellulose), while the volatilizable fraction of biomass could also be treated as a lumped component for the heterogeneous oxidation reaction. For each component considered, the same activation energy could be used, regardless of which biomass it appeared in. Within the range considered, the oxidation reaction could be described with an activation energy of $E_a = 130 \text{kJ mol}^{-1}$ and reaction orders in oxygen between 0.4–0.5 (dependent on the biomass). Differences between the biomasses were modelled by the pre-exponential factor $k_0$ and the reaction order in the solid conversion. It was further found that the reactivity of the different biomasses could to some degree be related to its composition: biomass rich in extractives had increased mass loss rates at low temperatures (<470 K), while biomasses rich in potassium (in the inorganic fraction) had high reaction rates above 500 K.

Lab scale experiments on loosely packed dust beds (10–40 g) were carried out to gain a further understanding of the ignition process. Onset of oxidation reactions was detectable by low concentrations of CO and CO$_2$ from around 373 K, which gradually increased with temperature. Larger sample bulk densities and higher ambient oxygen concentrations favored thermal runaway of the samples, which could otherwise (i.e., under ‘subcritical’ conditions) also stabilize and slowly oxidize. Critical conditions for thermal runaway mainly depended on the material tested. Qualitatively, the ignition behavior of the biomasses tested in this part of the study agreed with the thermogravimetric data: Sunflower and pine showed an early reaction onset, while the reactivity of beech and wheat increased towards higher temperatures (>500 K). Both experimental results as well as estimate calculations suggest that ignition was mainly kinetically controlled in the experiments. Acceleration of reactions on thermal runaway may be linked to a rapid increase in oxidation of the cellulose component.

A one-dimensional numerical model was developed to describe self-heating and ignition in dust beds, including reactions, mass and heat transfer. The reaction mechanism derived from thermogravimetric analysis was used in the model, while values for material property parameters could be found in the literature. Central aim of the model is to predict critical temperatures for ignition under different conditions. The lab scale experiments could be simulated with good accuracy, where ignition temperatures where predicted 2–5% lower than measured. No parameters were fitted to fixed bed experiments. Sensitivity to various parameters used in the model was investigated.
Onset of thermal runaway appeared to be controlled to a great extent by the kinetics of the oxidation reaction. Material properties, in comparison, had a very low influence. Further simulations were carried out to investigate effects of sample size and oxygen availability. Increasing the characteristic length scale or the bulk density of the sample drastically lowered the predicted ignition temperatures (as low as 395–460 K for large/dense samples). Thus, the scaling study demonstrated that self-ignition of settled biomass dust beds could plausibly explain mill fires.

In summary, self-heating and self-ignition were studied both experimentally and numerically in this work. Results show that critical conditions for self-ignition can be predicted based on the reaction kinetics of heterogeneous oxidation of the biomass. The kinetics of the oxidation reaction can to some degree be tied to the structural composition of biomass, and it is suggested that further research be carried out to investigate this link.
Dansk resumé


Ekspereimenter med enkle træpiller (0.25 g) indikerede, at heterogen oxida- tion af biomasse er den primære årsag til brand i kraftværkspærre. Små træpiller brød spontant i brand, når de blev udsat for temperaturer af ca. 500 K eller højere. Selvantændelsen medførte en stor stigning i temperatur (thermal runaway), udledning af større mængder af CO og CO₂, og en nærmest fuldstændig konvertering af det organiske materiale. Selvantændelse ved lav temperatur var forskellig fra flammende forbrænding. Flammer opstod kun, hvis temperaturen i reaktoren var højere end 700 K. Ud fra kulstofbalancen var det muligt at konkludere, at der sideløbende med oxidationen foregik en pyrolyse af biomassen. Begge processer foregår sandsynligvis i lignende omfang og med lignende hastighed.

En simpel reaktionsmekanisme blev udviklet til at beskrive parallel oxida- tion og pyrolyse af biomasse ved lave temperaturer. Mekanismen er baseret på sammensætningen af biomassen, og skelner mellem de volatile andele af henholdsvis ekstraktstoffer (fx fedsyrer) hemicellulose, lignin og cellu- lose, samt koks (den ikke-volatile andel). Seks biomasser, bøg, fyr, hvede
halm, solsikkefrø-skaller, og to typer af træpiller, blev analyseret. Parametrene af reaktionsmekanismen blev bestemt i termogravimetriske forsøg, som blev foretaget i flere isoterme trin mellem 423–523 K. De kinetiske modeller stemte godt overens med data, og kunne også til en vis grad ekstrapoleres til højere opvarmningshastigheder (5 K/min) og temperaturer op til 550–650 K. En model med fire komponenter (ekstraktstoffer, hemicellulose, lignin, cellulose) var nødvendig for pyrolyse, mens oxidation af den volatile andel af biomassen kunne beskrives ved en enkel reaktion. Uanset hvilken biomasse, der blev undersøgt, var det muligt at benytte den samme aktiveringsenergi for enhver komponent (henholdsvis ekstraktstoffer, hemicellulose, lignin, cellulose for pyrolyse, og den samlede volatile andel for oxidation). Oxidation af den volatile andel havde en fast aktiveringsenergi af $E_a = 130 \text{kJmol}^{-1}$ og en reaktionsorden i oxygen mellem 0.4–0.5 (afhængigt af biomassen). Forskellene mellem biomasserne blev modelleret i den prækspontentielle faktor $k_0$ og i reaktionsordnerne. Det viste sig derudover, at reaktiviteten af de forskellige biomasser delvist kunne forklares med deres sammensætning: Biomasse, der indeholder større mængder af ekstraktstoffer, havde højere reaktionshastigheder ved lavere temperaturer (<470 K), mens biomasse med stor indhold af kalium (som uorganisk andel) viste højere reaktionshastigheder ved 500 K og derover.


I dette studie blev selvopvarmning og selvantændelse undersøgt både med eksperimentelle og numeriske metoder. Resultaterne viser, at kritiske forhold for selvantændelsen kan forudsiges baseret på reaktionskinetikken af den heterogene oxidation af biomassen. Selve kinetikken er til en vis grad bestemt af biomassens strukturelle sammensætning, og det anbefales, at dette forhold undersøges yderligere.
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1. Introduction

1.1. Background and structure of this thesis

In the past years, interest in converting pulverized fuel power plants from coal- to biomass firing has increased. For pulverized fuel burners, the fuel is transported in pieces or chunks and milled on site. The fine fuel dust is then transported through ducts using a part of the air stream. Coal mills are usually operated at elevated inlet air temperatures with heat recovered from flue gas. As it is known that biomass will ignite at lower temperatures than coal, the temperature on the inlet is drastically reduced, by several 100 K, to prevent mill fires. This entails a lower rate of heat recovery, rendering power generation less efficient.

Pulverized coal firing can be considered a mature technology. There has also been a large amount of research on how burners, boilers and flue gas treatment can be altered to accommodate for the different fuel properties of biomass and coal. Storage and processing of granular biomass has also been investigated, especially for applications in the agriculture and food industries, e.g. silo storage of grains.

Mill conditions fall somewhat in between these two areas of research: operating temperatures in mills are higher than in storages, while residence times are shorter. Compared to boiler conditions, temperatures are much lower in mills, while residence times are much longer. It is argued in this thesis that mill fires are caused by spontaneous ignition of settled biomass dust, and therefore are comparable to storage fires. It is then argued that these types of self-ignition problems can largely be reduced to a question of finding appropriate reaction and heat release kinetics.

The thesis consists of the following chapters:

In Chapter 2, this work is set into context of the available literature. Previous knowledge on mill fires is briefly summarized. It is argued that self-ignition of settled fuel dusts is the most probable reason for mill fires. Experimental and theoretical methods to investigate self-ignition are briefly summarized. Biomass as a material is characterized. On the basis of this
literature studies, four questions are formulated, which form the program for this thesis.

In Chapter 3, an experimental study on ignition of single biomass pellets is presented. It is found that heterogeneous oxidation and pyrolysis are the dominant reactions at conditions leading to self-ignition.

In Chapter 4, a reaction mechanism for low temperature oxidation and pyrolysis is developed. Parameters of the mechanism are determined for six biomasses by thermogravimetric analysis. Reaction kinetic behavior is discussed in relation to the materials’ composition. A version of this chapter was under review at the time of writing, and has since been published in *Energy and Fuels*.

In Chapter 5, lab scale experiments on loosely packed dust beds are presented. Influences of biomass, bed packing density and oxygen availability are examined and discussed. Experiments presented in this chapter are also used for model validation.

In Chapter 6, modelling of fixed bed self-heating and self-ignition is presented. This chapter builds on results from the previous parts of the thesis. It is demonstrated that the lab-scale experiments from the previous chapter can be modelled with good accuracy, based on the kinetic mechanism developed in Chapter 4 and literature correlations for heat and mass transfer. Scaling of the model is further investigated, and it is found that mill fires may plausibly be explained by self-ignition of settled biomass dust. As it contains the central results of this thesis, this chapter, together with elements from the preceding chapter, is currently prepared for submission to a peer-reviewed journal.

In Chapter 7, the main results obtained in this work are summarized, and suggestions for future work are made.

### 1.2. Publications

Work presented in this thesis is also being prepared for publication in peer-reviewed journals. Intermediate results and work-in-progress has been presented at several conferences.

**Journal publications**

pp. 8606–8619, 2019. DOI: 10.1021/acs.energyfuels.9b00848


**Oral presentations including conference proceedings**


**Oral presentations without conference proceedings**


**Conference posters**


**Co-supervised MSc-thesis**

The following MSc-thesis was co-supervised as part of the PhD-studies:

2. Literature review: Biomass as a fire hazard in power plant mills

In the following, the background of this work will be presented. The chapter covers the use of biomass for heat and power generation, technology of pulverized fuel fired plants, and milling technology. It is argued, based on open literature, that mill fires can mostly be traced to super-critical self-heating, that eventually leads to ignition. Theoretical and experimental treatment of self-heating and self-ignition is then reviewed, showing that the state of the art in self-ignition modelling relies on highly simplified reaction mechanisms. It is then argued that biomass is a structurally complex and inhomogeneous material, which is not well represented by such simple models. The motivation and program for this thesis is then outlined based on this argumentation.

To avoid excessive doubling, the more specific literature that forms the background of this work (e.g. on reaction kinetic mechanisms or on detailed self-heating models) is reviewed in the corresponding chapters of this thesis.

2.1. Use of biomass for heat and power generation

There is an increasing demand to replace fossil fuels, such as coal, oil and natural gas, by renewable energy sources. Biomass is an interesting option, as is can be integrated into existing heat and power generation systems. Unlike other renewables (e.g., wind or solar energy), biomass can be easily stored and converted to electricity or heat when demand arises. The use of biomass for large-scale heat and power generation has been extensively researched. As a technology, it is currently nearing a mature state. There are several demonstration projects and some few commercial, full-scale operations with biomass.

2.1.1. Biomass in the energy sector

Biomass is a generic term for fuels derived from natural organic matter. While this definition is sometimes limited to plant material [1], broader definitions may also include animal waste and algae. In this sense, sources in-
Biomass as a fire hazard in power plant mills

Inclusion agriculture, forestry, fishery and aquaculture, and municipal and industrial waste [2,3]. As of 2012, Biomass makes up 62% of all renewable energy consumption in the EU (8.7% of total energy consumption in the EU) [4]. The corresponding figures on a worldwide scale are 77% share of all renewables and 10% of total primary energy (2009) [3]. The most widely used biomass materials in the power and heating sector are wood or wood-derived [3–5]. At current, the price per unit energy of biomass is higher than that of coal, oil and gas [6]. The use of biomass as an energy source in highly industrialized countries is therefore largely driven by legislation which is shaped by environmental concerns. These are usually national policies or international agreements that are implemented in national laws – this means that the use of biomass for energy differs from country to country.

Biomass typically has a lower energy density and is collected from a larger area than conventional fossil fuels. Therefore, pre-processing methods have been developed to increase the specific heating value of biomass fuels. These measures increases transportation efficiency both from harvesting site to processing plant as well as within a processing plant, as less inert material needs to be moved [4,5,7]. Pre-treatment methods can be divided into three groups: mechanical treatment, e.g. briquetting or pelletizing; biological treatment, e.g. by anaerobic bacteria; and thermal treatment (pyrolysis/torrefaction). According to an IEA report [3], only pelletization is commercially employed as a densification technique, while other treatments are still in research or demonstration phase.

For industrial-scale heat and power generation, solid biomass can be combusted either alone or in combination with other fuels, such as coal or municipal solid waste. Activity in the field generally concentrates on the EU and the US with minor activities in Australia, Canada and south-east Asia [7,8]. Large-scale applications (>10 MW thermal capacity) of biomass combustion can be found especially in Denmark, Sweden, Finland, Germany and the United Kingdom [9,10]. In co-firing plants, the share of biomass is usually limited due to lower fuel quality, lower by-product quality, deposition formation and corrosive behavior, as well as impact on flue gas cleaning equipment [7]. Biomass shares reported in the literature are typically around 5–10% on energy basis [3,5,7,8]. The majority of European co-fired utility boilers use pulverized fuel burners, followed by fluidized bed and grate fired boilers [8]. The technology favored varies form country to country and depends on the regional supply of fuel and demand of energy.

Alternatively, existing power plants can be adapted to full biomass firing, which usually entails greater modifications of equipment and process parameters. It also places some restriction on the fuel used: full biomass fir-
ing requires low ash content and mild slagging and/or corrosive behavior, which is why only wood is used in 100% biomass firing [10]. The first pulverized coal fired power plant to be successfully converted to wood pellet firing was Hässelbyverket in Sweden [11]. Further case studies on full coal-to-biomass conversion of power plants are reported from the United Kingdom, the Netherlands, and Denmark [10,12].

2.1.2. Situation in Denmark

Denmark plans to have phased out coal and oil for heat and electricity generation by 2035 [13]. As can be seen from Table 2.1, fossil fuels still had a major role in thermal power plants in Denmark in 2016. With the exception of Fyn 8, all of the larger biomass-fired units listed in Table 2.1 are pulverized fuel boilers, while smaller, decentralized units are commonly grate fired (see [14]). It is planned to convert the centralized coal fired plants to full biomass firing [6]. At the time of writing, this had been carried out at Studstrupværket and Avedøreværket, and work was under way at Amagerværket. All of the larger thermal power plants are combined heat and power plants, and it is expected that their operation mode will shift to heat-demand driven operation within the near future [6]. The installed capacity of central thermal power plants is moreover expected to decrease from cur-

Table 2.1.: Thermal power plants in Denmark, 2016 [6]

<table>
<thead>
<tr>
<th>Unit</th>
<th>Pe [MW]</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amagerværket 1</td>
<td>70</td>
<td>wood pellets, oil, coal</td>
</tr>
<tr>
<td>Amagerværket 3</td>
<td>250</td>
<td>coal, heavy oil</td>
</tr>
<tr>
<td>Asnæsværket 2</td>
<td>140</td>
<td>coal, heavy oil</td>
</tr>
<tr>
<td>Avedøreværket 1</td>
<td>255</td>
<td>coal, oil; wood pellets(^1)</td>
</tr>
<tr>
<td>Avedøreværket 2</td>
<td>545</td>
<td>wood, coal, oil, straw</td>
</tr>
<tr>
<td>Esbjergværket</td>
<td>370</td>
<td>coal, oil</td>
</tr>
<tr>
<td>Fynsværket 7</td>
<td>380</td>
<td>coal</td>
</tr>
<tr>
<td>Fynsværket 8</td>
<td>35</td>
<td>straw</td>
</tr>
<tr>
<td>H. C. Ørstedsværket 7</td>
<td>75</td>
<td>natural gas</td>
</tr>
<tr>
<td>H. C. Ørstedsværket 8</td>
<td>25</td>
<td>natural gas</td>
</tr>
<tr>
<td>Herningværket</td>
<td>90</td>
<td>wood chips, wood pellets, natural gas</td>
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<tr>
<td>Nordjyllandsværket 3</td>
<td>380</td>
<td>coal</td>
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<tr>
<td>Skærbækværket 3</td>
<td>390</td>
<td>natural gas</td>
</tr>
<tr>
<td>Studstrupværket 3</td>
<td>360</td>
<td>coal, oil, straw; wood pellets(^1)</td>
</tr>
<tr>
<td>short-term reserve, sum</td>
<td>495</td>
<td></td>
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<tr>
<td>mid-term reserve, sum</td>
<td>1260</td>
<td></td>
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<tr>
<td>conserved, sum</td>
<td>1230</td>
<td></td>
</tr>
<tr>
<td>Decentralized stations, sum</td>
<td>2495</td>
<td>various(^2)</td>
</tr>
</tbody>
</table>

\(^1\) Conversion to wood pellet firing planned for 2016/2017
\(^2\) 61% natural gas, 15% diesel and oil, 10% biomass and 14% waste; by installed capacity
rently 3860 MW to less than 2000 MW by 2040. By comparison, the installed capacity of wind turbines is 5080 MW as of 2016 (75% of which is land-based) and expected to increase.

2.1.3. Technology of pulverized fuel fired power plants

Figure 2.1 shows a simplified setup of a pulverized fuel boiler. Fuels arrive at the power plant in form of large pieces – as larger chunks in the case of coal, or typically as pellets in the case of biomass. Storage, transport and handling of such larger particles is generally easier than fine particle dusts. For this reason, biomass grains, fibers and dust particles are pressed into pellets for transportation. Wood pellets have a higher solid density (1100–1350 kg m\(^{-3}\)) [15–17] than fresh wood (200–1000 kg m\(^{-3}\)) [17–19]. Mills in power plants are used to increase the specific surface area of the fuel. With a larger area for oxygen access, heat transfer and release of volatiles, combustion reactions can proceed more rapidly in the boiler. A secondary function of mills is the drying of fuels. As the dust particles are easily entrained in airflow, pneumatic transport is used between mills and burners. A heat exchanger between flue gas and fresh air is used to pre-heat combustion air. Pre-heating combustion air is a method of recovering heat otherwise lost to the surroundings. A part of this air stream is directed to the mills, where it is used as a carrier gas to transport the pulverized fuel to the burners. In some boilers, part of the flue gas is recirculated to control flame temperature and emissions (not shown here).

Mills can be classified by their operating speed [20] or by their working principle [21] (e.g., impact mills, roller mills and ball media mills). Low

\[ 	ext{Figure 2.1.: Simplified power plant diagram. Flue gas recirculation and steam cycle not shown.} \]
speed mills are robust but have a high specific power consumption, whereas medium speed mills (e.g. vertical roller mills, vertical spindle bowl mills and ring-and-ball mills) are considered more economically advantageous [20]. Figure 2.2 shows the simplified layout of a vertical roller mill, such as is commonly used in Danish pulverized fuel-fired power plants. Fuel falls from the vertical feed pipe on to a rotating table, which is powered by an external motor (not shown in Fig. 2.2). Larger fuel particles are crushed between the mill table and spring-loaded rollers. The particle sizes of milled wood pellets are often lower than the particles the pellets are composed of [22, 23]. Particles of sufficiently small size are entrained by hot air sweeping upwards past the mill table. In the classifier, small particles are allowed to pass to the outlet duct, whereas larger particles are returned to the grinding table. Additional cold air is used to control the temperature of the mills [12, 20]. The mill air inlet temperature is otherwise determined by the efficiency of the heat exchange between fresh air and flue gas.

Re-using the existing coal mills (as opposed to replacing them by dedicated biomass mills) has several economic and operational advantages [10], among them low investment costs and familiarity of the equipment to operator staff. Typically, coal mills have to be mechanically modified for use with biomass such as wood pellets [10, 12, 23, 24]. This may include modified classifiers [10, 12, 24], installation of (modified) dam rings [12], drilling holes into the roller

![Figure 2.2: Schematic of a vertical roller mill.](image-url)
track and fitting the rollers with materials of higher hardness [23]. Figure 2.3 shows the inside of a mill used for wood pellets, opened for maintenance. Residual dust and pellets have been removed.

2.2. Mill fires

Fires in power plant mills have not received much attention from the scientific community. More findings have been published in non-academic journals and in technical reports. Most of the available material deals with incidents in mills used for coal. Two types of accidents are reported, fires and explosions. Explosions are characterized by a sudden and significant pressure rise on ignition [25]. In surveys of coal mill accidents, the term explosions has been used for incidents where structural deformation or containment breach occurred [26]. Fires may precede or follow explosions, but explosions can also occur independently in mills [27,28]. In a survey of 1700 pulverizers at 360 plants [26,27], not all fires resulted in an explosion, but all explosions were initiated thermally (as opposed to e.g. sparks). As a source of dust explosions in the process industry, mechanical sparks are also rare; and surfaces heated by friction are seen as more likely ignition sources [29]. Fires occurred at higher frequency than explosions [26]. Fires and explosions in mills are often linked to transient operating conditions, such as shutdown or restart [27,28].

2.2.1. Causes and detection of mill fires

It is generally thought that self-ignition of dusts settled in power plant mills are the cause of fires [12,28,30–34]. The same has been observed for fires in coal firing systems in the cement industry [35]. This is either due to long
residence times of such dust accumulations [30,31,33,34] or to the elevated
temperatures of air and/or surfaces in mills [12,30]. Alternative hypothe-
ses that are discussed are ignition by over-heating during grinding [36], or
sparks from loose metal objects in the fuel stream [32,36]. Tribo-electric
charge generation when handling or processing wood pellets (not restricted
to power plant mills) has been also been investigated as a cause of explosion
or fires [37]. Wood pellet dusts were seen to accumulate higher charges (per
mass) than coal in the aforementioned study, indicating a greater ignition
risk.

Ignition by sparks and by hot objects has been investigated in lab scale ex-
periments [38-41]. Igniting fires in settled dust beds (among other materi-
als of wood, cellulose, cotton and starch) by sparks required repeated spark
showers [38], which makes this an unlikely root cause of mill fires. Similarly,
igniting dust beds by hot foreign objects requires these bodies to be either
large or have a high temperature: Ignition of pulverized grass blends by hot
metal spheres in the lab required temperatures of 973 K at 1.5 mm diameter
and 793 K at 8 mm diameter [39]. To initiate smoldering in cork or beech
wood dusts by hot bodies of 573 K, spheres of 40 mm were necessary [40].
Similar combinations of object size and temperature are reported for igniting
wood and corn starch dusts [41].

Smoldering nests of dust particles may either themselves turn into fires [34,
41], or cause dust explosions [25, 29, 32, 36]. Experiments carried out by
dropping smoldering nests in silos filled with dust/air mixtures [41,42] showed
that temperatures required to ignite the surrounding suspended dust were
relatively high (>973 K). Dropping smoldering nests of cork or wood dust in
empty silos showed such nests to readily begin flaming, however [41]. Smol-
dering dust accumulations in confined spaces may also release volatile gases,
which may then ignite [25]; however, this has not been explicitly reported in
the context of mill fires. Auto-ignition temperatures of typical combustible
volatiles in air are much higher than mill operating temperatures (H₂: 858 K,
CO: 878 K, CH₄: 868 K, C₂H₆: 788 K and C₃H₈: 743 K [43-45]). This would
imply the presence of an external ignition source (spark, hot surface, or the
smoldering fire itself). Lower explosion limits of alkanes are in order of 1–5 %
by volume (in air) [45]. In order to reach such concentrations, relatively long
residence times would be necessary, as mills are more or less open to the en-
vironment and additionally have large headspace volumes.

Monitoring for carbon monoxide has been suggested to detect the onset of
smoldering coal mill fires [30,32], and for smoldering particle nests in gen-
eral [42]. Monitoring only temperature rise is seen as insufficient [30,32].

Of the above, smoldering fires in settled dust beds would best explain the ob-
served higher frequency of mill fires following shutdown and restart. Overheating during grinding should lead to mill fires occurring more frequently during peak load operation or in connection with mechanical failures in the mill (e.g. blockage). Sparks, especially those generated by foreign objects, would lead to more randomly occurring mill fires.

### 2.2.2. Mill fires at Avedøreværket: a case study

Avedøreværket is a combined heat and power plant with a production capacity of 810 MW electricity and 900 MW heat. The plant consist of two blocks. Block 1 was commissioned in 1990 as a coal and heavy fuel oil fired boiler, but is now converted to wood pellet firing. Block 2 was built in 2001 and has a modular layout. The main boiler is fired with natural gas, oil and pulverized wood pellets. A second, straw-fired boiler supplies steam to a common turbine system. A gas turbine is used for peak load. Its exhaust gases are also used to supply heat to the common steam system.

The mills have a mechanical power of 8–10 kW/t of fuel, most of which is dissipated as heat in grinding. Currently, the system is operated with inlet air temperatures of 398 K (125 °C). The outlet stream (air and ground particles) has a temperature of 343 K (70 °C). Both temperatures are monitored. Furthermore, pressure gauges are used to detect an explosion in the mill, which leads to an automatic shutdown and the release of NaHCO$_3$ extinguisher powder.

The mill air inlet temperature was set to 403 K (130 °C) when the plant was first operated with biomass in 2003. Fumes and tars or oils seeping from the mill however indicated a slow thermal conversion, so that the inlet temperature was drastically lowered to 358 K (85 °C). The plant remained in operation with this setting for eight years. As experience from other plants indicated that higher temperatures were permissible, the inlet temperature was raised again to its present level (398 K). Since then, there has been less than one mill fire incident per year. Trials with even higher inlet temperatures were not successful and led to an explosion (Mill 30 at 423 K) or a fire with 6 hours delay (Mill 10 at 413 K). In contrast, mills at a similar plant (Studstrupværket) are operated at air inlet temperatures of 423 K [12]. There is anecdotal evidence of this plant being able to run at inlet temperatures of up to 443 K (170 °C)$^1$. Both facilities have vertical roller mills. Mill fires appear to follow a common sequence:

1. An event unrelated to mill operation results in rapid shutdown of burner and mill.

---

$^1$Personal communication
2. Fuel remains on the grinding table. Any airborne fuel will also settle in the mills.

3. After a shutdown time of 2–3 days, the mill is restarted and back in operation.

4. With a delay of 10–24 hours$^2$, an ignition in the mill is detected by a sudden pressure rise. The mill outlet temperature does not show any significant rise until then.

5. The ignition and the following fire lead to an automatic shutdown of the mill. The remaining fuel is sprayed with NaHCO$_3$ as extinguisher.

A local investigation pointed to smoldering fuel accumulations as a likely cause of the fires. During normal operation, a fuel bed of approximately 50 mm is present on the mill table. After a sudden mill shutdown, this layer thickness would be increased due to settling of particles. Due to the internal design of the mill, flat surfaces exist on which dust accumulations may build up (Figure 2.4). There is currently no understanding of whether these dust beds are stable in normal operation mode and how long they persist.

Three incidents were specifically pointed out, two of which may be linked to a smoldering or burning fuel accumulation:

- In the first case, a loss of cold purge air near the grinding rollers led to a local ignition.
- A scraper below the mill table was not installed correctly and left a 30 mm bed layer, which ignited. Contrarily, the 1 mm bed height seen in normal operation has not caused any problems.
- An immediate fire occurred after uncontrolled air dampers leaked hot

$^2$ later reported as >24 hours

![Figure 2.4.: Potential dust accumulation sites in mills](image-url)
Based on the above experience, any large dust accumulations are considered as a potential source of fire. A cleaning routine has been developed: whenever a longer standstill of the mill is expected, it is manually cleaned from all deposits by use of a vacuum cleaner. During mill shutdown, one of four purge air lines remains open, blowing cold air into the system.

### 2.3. Self-heating and self-ignition

The above studies and operator experience suggests that self-heating plays a key role in the development of mill fires – either directly via overheating and self-ignition, via sudden entrainment and dispersion of smoldering dust beds on mill restart, or via release of combustible volatiles. Theories that explain self-ignition as a super-critical case of self-heating are available in the literature. These will be discussed first in the following, beginning with the classical theories of Semenov [46, 47] and Frank-Kamenetskii [48], followed by further developments in the field. Experimental studies of several researchers have built on these theories, both to explain observations and also to make predictions of self-ignition in industrial scale samples. Some aspects of these studies are summarized following the discussion of the theoretical frameworks. In the last part of this section, some alternative methods of characterizing self-heating and self-ignition will be reviewed.

#### 2.3.1. Self-ignition theories of Semenov and Frank-Kamenetskii

The most widespread theories of self-ignition were originally derived for explosive, binary mixtures of gases [46–49], but have since also been applied to combustible solids. The European norm to determine self ignition of settled dust particles, EN 15188 [50], is directly based on such a theory of thermal explosions [48]. A simple theory of thermal ignition was first set forth by van’t Hoff, who argued that within a combustible gas mixture, a reaction will maintain itself when heat release by the reaction equals or exceeds the heat loss to the environment [49]. A mathematical formulation of this idea was first presented by Semenov, who was at the time unaware of van’t Hoff’s work [46, 47]. The principle of Semenov’s theory is that while external heat transfer $\dot{Q}_L$ is governed by a linear law in temperature,

$$
\dot{Q}_L = \alpha \cdot A \cdot (T - T_\infty)
$$

(2.1)
reaction heat release $\dot{Q}_R$ increases exponentially with temperature. It can be modelled by an Arrhenius type equation:

$$\dot{Q}_R = H_R \cdot k_0 \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (2.2)$$

In the above, $\alpha$ is the heat transfer coefficient, $A$ the surface area and $T_\infty$ the temperature of the surroundings. The heat of reaction is $H_R$, and $k_0$ and $E_a$ are the coefficients of the Arrhenius expression. The stability criterion by Semenov is based on the relative increase in heat release and heat dissipation rates, if the two become equal for a given temperature. Systems that become unstable and undergo thermal runaway have a faster increase in heat release with temperature than the increase in heat dissipation. The separation of stable, stationary reactions and and unstable systems (thermal runaway) can be described at a critical temperature. Systems at the critical point for self-ignition fulfill the following conditions [46]:

$$\dot{Q}_R(T_{\text{crit}}) = \dot{Q}_L(T_{\text{crit}}) \quad \text{and} \quad \left. \frac{d\dot{Q}_R}{dT} \right|_{T_{\text{crit}}} = \left. \frac{d\dot{Q}_L}{dT} \right|_{T_{\text{crit}}} \quad (2.3)$$

For given reaction and heat-transfer properties ($k_0$, $E_a$, $H_R$ and $\alpha$), this can e.g. be used to calculate critical ambient temperatures $T_\infty$.

Critical conditions for ignition and scaling laws can be demonstrated in a simple diagram, Figure 2.5. Mass specific heat transfer and heat release rates $\dot{q} = \dot{Q}/m$ are used in the following, as this helps illustrate scaling effects. In the base case, a system initially in thermal equilibrium with its surroundings ($\dot{q}_L = 0$) at temperature $T_0$ will gradually heat up due to reactions, as $\dot{q}_R > \dot{q}_L$. The system will then reach a point at which heat release and heat dissipation are equal. Any further increase in temperature would lead to heat loss increasing faster than heat generation, and the system stabilizes at the temperature where heat dissipation and heat release are equal. If the same system is initially at a higher temperature $T_1$, it will also gradually heat up - corresponding to the shift (a) of the heat loss curve to $\dot{q}_{L1,\text{crit}}$. At the temperature of equal heat release and heat dissipation, the system is now no longer stable: Any increase in temperature would lead to more heat release than can be dissipated. The behavior at this point is catastrophic, i.e. a minor temperature increase will rapidly accelerate to a thermal runaway. For initial temperatures higher than $T_1$, no equilibrium point exists, and the system is unconditionally unstable.

If the mass of the system is increased and the reaction remains the same (shifting the mass loss curve by (b) compared to the base case), it will become unstable at lower temperatures. This happens because the heat dissipation occurs over the outer surface area and scales with the square of a charac-
Figure 2.5.: Ignition theory by Semenov [46], adapted. Mass-specific heat \( \dot{q} = \frac{Q}{m} \) is used in this plot to illustrate scaling with sample size.

Frank-Kamenetskii, a co-worker of Semenov, presented an alternative theory of self-ignition [48]. He argued that the heat transfer within the system is more relevant than the external heat transfer. While Semenov considered temperature to be uniform within the system (a mixture of combustible gases), Frank-Kamenetskii used an approach assuming that explosion is controlled by temperature differences within the system. The argumentation is based on the observation that ignition usually does not occur homogeneously throughout the mixture, but localized. The heat balance for the Frank-Kamenetskii theory can therefore be formulated as:

\[
-\lambda \cdot \Delta T = H_R \cdot k_0 \cdot \exp\left(-\frac{E_a}{RT}\right)
\]  

(2.4)

where the left-hand side is heat conduction according to Fourier’s law (\( \lambda \) is the thermal conductivity and \( \Delta \) is the Laplace-operator) and the right-hand side is the heat release due to reaction (heat of reaction per unit volume, multiplied by the Arrhenius-term). Re-arranging and formulating the problem in terms of a non-dimensional temperature \( \theta \) and a dimensionless length

\[\frac{\lambda}{R} \] 

originally published 1938, in Russian
scale $\xi$, Frank-Kamenetskii arrived at the dimensionless equation

$$\Delta_{\xi} \theta = -\delta \cdot \exp(\theta)$$

(2.5)

The index $\xi$ on the Laplace operator shows that the gradient is expressed in dimensionless coordinates. In this equation, $\delta$ is the only free parameter and contains all physical properties of the system:

$$\delta = \frac{H^2}{\lambda} \cdot \frac{E_a}{R \cdot T_0^2} \cdot L^2 \cdot k_0 \cdot \exp\left(-\frac{E_a}{R \cdot T_0}\right)$$

(2.6)

In this equation, $\lambda$ is the thermal conductivity and $T_0$ is a characteristic temperature near ignition conditions. Frank-Kamenetskii argued that there are critical values of $\delta$, for which solutions of equation 2.5 exist. For $\delta > \delta_{\text{crit}}$, there is no stationary solution, indicating a thermal runaway. Solving equation 2.5 for an infinite layer, an infinite cylinder and a sphere, Frank-Kamenetskii arrived at values of $\delta_{\text{crit}} = 0.88$, 2.00 and 3.32, respectively.

Some further assumptions that underly the self-ignition theories are that the reaction is zero order in the solid (i.e. consumption of reactants does not need to be accounted for); reactants are well-mixed and there are no mass transfer limitations; material properties are constant; a single reaction takes place, which is the cause for self-heating and eventual thermal runaway; heat dissipation is governed either by external heat transfer (Semenov) or internal heat transfer (Frank-Kamenetskii); and no other heat sources or sinks exist. Moreover, classical self-ignition theories are valid for stationary systems only, and cannot explain processes with dynamic heating or cooling [51].

2.3.2. Further developments in self-ignition theory

Several authors have proposed modified ignition theories to account for the simplifications in Semenov’s and Frank-Kamenetskii’s theories. Thomas [52] developed modified critical parameters $\delta_{\text{crit}}$ for cases in which both external and internal heat transfer are relevant. In this treatment for arbitrary Biot-numbers, the original theories represent the two limiting cases, depending on whether external or internal heat transfer is limiting, i.e. $\text{Bi} \to 0$ (Semenov) or $\text{Bi} \to \infty$ (Frank-Kamenetskii). Kordylewski and Wach [53] present modified Frank-Kamenetskii $\delta$ parameters to account for reactant consumption. Further analysis of the effect of reactant consumption was presented by Boddington et al. [54]. They demonstrate that deviations from the no-consumption solution are greater for systems with low exothermicity ('dilute systems'). Thomas and Bowes [55] pointed out that the reaction showing initial self-heating need not be the one leading to thermal runaway. A the-
Biomass as a fire hazard in power plant mills

oretical treatment of this case is presented by Bowes [56], accounting for systems in which a minor component releases enough heat to trigger thermal runaway of a major component. Examples given for such systems include organic matter with oil or fat content, e.g. oily fibers, fishmeal, but also wood fiber insulation board.

Chen and Chong [57, 58] developed the crossing-point method to describe transient self-heating in porous solids. Instead of a critical ambient temperature, their model defines a crossing-point temperature as a characteristic quantity for self-ignition. Instead of Frank-Kamenetskii’s steady-state heat balance, the transient heat balance is solved for a one-dimensional, symmetric geometry:

\[
\rho c_p \frac{\partial T}{\partial t} = \lambda \cdot \Delta T + H''_R \cdot k_0 \cdot \exp\left(-\frac{E_a}{R \cdot T}\right)
\]  \hspace{1cm} (2.7)

The crossing point temperature \( T_{cp} \) is defined as that temperature, at which the heat conduction term \( \Delta T \) (where \( \Delta \) is the Laplace operator) becomes zero at the symmetry locus. The authors argue that activation energy and heat release rate can then be calculated from \( \frac{\partial T}{\partial t} \) evaluated around \( T_{cp} \).

2.3.3. Self-ignition based on isothermal and transient oven experiments

Several researchers have used the theories outlined above as a framework for experimental investigations. Critical temperatures for self-ignition of pulverized materials have been determined experimentally for lab scale samples. Procedures used include isothermal oven tests, transient heating oven tests, and hot plate tests. Scaling laws have then been used to make predictions of critical ambient temperatures for industrial processes.

2.3.3.1. Effects of sample size and mass

Most investigations aimed at establishing critical conditions for certain materials, among these mainly coal, lignite, wood dust, foodstuff, and various commodities. Some experimental data available in the literature are compiled in Figure 2.6. All of the data points were taken from isothermal oven experiments [59–67], where a wire-mesh basket holding the sample is subjected to a constant temperature for a prolonged period of time. Some authors [61–63] explicitly refer to the European norm EN 15188 [50]. The majority of the reported critical temperatures for self-ignition were measured in air. Some data-points for wood (sawdust) [59], as well as for lignite, cork,
Some trends can be identified in Fig. 2.6: For the same sample material, the critical ambient temperature $T_{\text{crit}}$ for self-ignition appears to decrease with increasing volume to area ratio of the bulk sample (i.e. the test basket). The scaling of critical temperatures with this characteristic length $L = V/A$ is expected from both Semenov’s [46] and Frank-Kamenetskii’s [48] theories of self-ignition. Biomass and other biogenic materials show slightly higher self-ignition temperatures than coal or lignite at the same volume to area ratio. Another feature of the chart is the relatively broad scatter of critical temperatures for similar materials. Two outliers are visible in Fig. 2.6 which are readily explained: one of them is the critical ignition temperature of cork dust in 1.3% oxygen atmosphere [66] and the other bagasse in a cylindrical basket with a high length to diameter ratio [64]. Scatter among the other data-points is however due to variations in material and experimental procedures. In Figure 2.6, data have been compiled by grouping similar materials, and by deliberately neglecting (among others) dust particle size, the shape of the bulk sample (i.e. the sample holder), and the bulk density of the sample. Especially the latter point is worthy of discussion. Unlike gases, were volume and amount of substance or mass are coupled via an equation of state (e.g., the ideal gas law), solid dusts can be compacted quite substantially. Com-
paction allows for varying mass within a volume, which can be expressed as different bulk densities. For reaction within a given volume, heat released scales with the amount of matter or mass. On the other hand, heat dissipation by external heat transfer (Semenov’s ignition theory [46]) depends on the outer surface area, i.e. an entirely geometric property. In Frank-Kamenetskii’s ignition theory [48], heat dissipation depends on the thermal diffusivity \( a = \lambda/\rho c_p \). The relationship between thermal diffusivity and bulk density is non-linear, as the overall density appearing in \( a \) is approximately that of the solid (skeletal) density, whereas the thermal conductivity is strongly influenced by the thermal conductivity of the interstitial gas and the contact or arrangement between solid particles. Unfortunately, bulk density or sample mass are not always reported. This makes it difficult to use literature self-ignition data in calculations, even if it is determined according to standard tests (e.g. EN 15188 [50]). From the above cited works, bulk density is available from [59, 60, 64, 66, 67]. Re-plotting the data shown in Figure 2.6 in terms of mass to volume ratio shows a slightly different picture. Since biomass typically has a lower density than coal and lignite, wood and biomass samples appear at a low mass to area ratio and higher critical temperatures, whereas coal and lignite are in the high mass to area ratio/low critical temperature region of the plot. Such an analysis was carried out as part of this work and can be found in [68]. While scaling with mass instead of with volume seems more appropriate, it does however not remove the scatter seen among similar materials in Fig. 2.6. Scaling of auto-ignition temperatures with mass in transient heating experiments is reported by Moqbel et al. [69], where the authors also find considerable uncertainties.

2.3.3.2. Effect of ambient oxygen concentration

Self-heating of dust accumulations was observed to be slow and proceed even under very low oxygen concentrations for wood, lignite, and other organic substances [59, 66, 69, 70]. Critical temperatures for self-ignition are however slightly increased when oxygen is reduced, Fig. 2.7. Temperature gradients and peak temperatures are lower under low oxygen concentration [59, 66, 69]. Therefore, the onset of self-ignition becomes increasingly difficult to define as oxygen concentrations drop below 6% [66]. Bowes and Thomas [59] report visible fumes and rapid heating of sawdust under ambient oxygen concentrations, and some discoloration of the sample and little smoke under low oxygen (4%) concentrations. This slow conversion could be sustained in a steady state for some time and was identified as diffusion-controlled regime by the authors. When suddenly exposed to ambient oxygen concentrations, such samples were found to rapidly char and later to
Figure 2.7.: Self-ignition data for different ambient oxygen concentrations, compiled from [59] (wood) and [66] (cork, detergent, lignite). The number in brackets refers to the volume to area ratio of the bulk samples, measured in millimeter.

Glow [59]. Spontaneous transition from smoldering under 10% oxygen to flaming when samples were exposed to 20% oxygen is also reported in [69]. For synthetic waste, e.g. paper, textiles, food; as well as actual municipal solid waste, some contributions of exothermal pyrolysis where observed, i.e. samples would self-heat even if no oxygen was present [69].

2.3.3.3. Moisture and humidity

Water, both as humidity in the gas phase and as moisture in the solid can influence self-ignition in several ways, some promoting and some inhibiting self-ignition [64]. Evaporation of water is endothermic and thus may act as a heat sink during self-heating [64, 71, 72]. Adding water to coal samples was found to reduce self-ignition temperatures [70, 72]. Possible explanations given are thermal (absorption, condensation) and mechanical (cracking of pores, thus increasing available surface area). For synthetic waste samples, no clear trend could be established [69].

2.3.3.4. Fuel properties

As is apparent from Figure 2.6, critical temperatures depend highly on the material type. Correlating data presented in the figure with fuel composition data from ultimate and proximate analyses (where such data are reported)
did however not allow to identify clear trends. Some findings from individual studies are nevertheless summarized below.

García-Torrent et al. [62] compared various biomass materials to coal. While no fuel composition is given, their results show that biogenic materials (animal waste, lycopodium, dry sludge, wheat) have a lower critical storage temperature and higher induction times than bituminous coal. On the other hand, Veznikova et al. [61] found bituminous coals and lignite more liable to self-ignition in storage piles than wood pellets or sawdust.

Among biomass samples, it was argued that the lignocellulose composition, rather than the elemental composition, determines reactivity. Samples with higher lignin content had an increased risk of self-ignition in lab scale tests [73]. In coals and lignite, the critical temperature for self-ignition was found to decrease with increasing volatile content [61, 72]. This trend does not appear to hold when coal is compared to biomass, however: Among the samples investigated in study [61], the two biomass fuels had the highest content of volatiles and the lowest content of both fixed carbon and ash. The sample assessed most liable to spontaneously combust was lignite, though [61]. A decrease in self-ignition temperatures with coal oxygen content was also reported [67].

2.3.3.5. Particle size

Particle size, as opposed to bulk sample size, is investigated only in few studies. In studies were particle size is not in the focus of the work, it is often omitted from the reported material data, making meta-studies difficult. Self-ignition temperature was found to increase with particle size in coals [67, 72]. How much critical temperatures varied with particle size was seen to depend on chemical properties of the coal (e.g., expressed as coal rank) in [67].

2.3.3.6. Ignition source, reaction propagation and extinction in dust beds

In the majority of the above studies, ignition was induced by exposing a sample to a hot environment (oven). Other types of ignition sources such as ignition by hot bodies and glowing nests of powders have also been investigated [40, 74, 75]. Both a minimum temperature and a minimum energy are needed for a hot body embedded in dust or a smoldering nest to ignite the dust sample. It is also pointed out that the two cases under investigation represent different time-dependent boundary conditions. While the glowing nest is a heat source that remains at an almost stationary temperature (heat loss is compensated by reaction), the hot body will lose heat and decrease in
temperature until thermal equilibrium is reached [40,74].

Once ignited, propagation of the reaction was independent from the ignition source [40]. Propagation velocity is determined by the properties of the material and also to a large degree controlled by mass transfer, i.e. the diffusion of oxygen to the reaction site and the transport of products away from it [74]. Even a low ambient oxygen content can be enough to sustain a smoldering reaction [59,75], but propagation velocity can then drop to low values (0.1 mm/min). Oxygen availability may control extinction, if reactions are fast enough to become diffusion limited [59].

2.3.4. Other methods of ranking self-ignition propensity

Other indices (besides the critical ambient temperature) to rank the risk of spontaneous ignition have been proposed as well [63,73,76,77]. Mainly, these are based on characteristic temperatures that can be read from lab scale experiments such as thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC). Some examples are temperature of maximum weight loss rate [63,76,77], onset temperature of exothermal reactions [63,73,76], apparent activation energy of oxidation [63,73], apparent activation energy of pyrolysis [77], or combinations of a characteristic temperature and an apparent activation energy [63,73,77]. Based on the literature record, these indices are not widely used, however, and data for different materials is scarce. Also, their applicability can be debated: the onset of exothermal reactions reported in [63,73,76] falls within the range of 343–383 K for most materials, so that it would likely be influenced by evaporation of moisture. The authors [63,73,76] do not discuss how these two effects can be distinguished in the thermograms presented. It could moreover be argued that apparent activation energy (of oxidation) and temperature of maximum weight loss rate are essentially parameters describing the reaction rate, where the former describes the change of reactivity with temperature, while the latter is a combination of the reaction rate, the applied experimental heating profile, and the degree of sample conversion.

Calorimetry is a method to measure heating rates, instead of measuring critical temperatures. Davis and Byrne [78] proposed an adiabatic calorimeter to measure self-heating of coals, where the temperature of the surroundings is controlled (by heating) to match that of the sample. A similar device is used in [33]. Heating rates can then be determined independently of heat losses and starting at very low temperatures (300 K [78], 313 K [33]). The method of actively heating the surrounding to the measured sample temperature requires very accurate control loops in order to not artificially induce
(or dampen) self-heating. The use of insulated vessels has also been proposed as an alternative adiabatic method [79, 80].

Isothermal calorimetry has been used to measure self-heating in wood pellets [81–83]. This method is typically applied at low temperatures (303–373 K), and measured mass-specific heating rates are in order of 0.01–1 mW g⁻¹ [81–83]. The method can be combined with gas concentration measurements to determine e.g. oxygen depletion rates. The apparent advantage of isothermal calorimetry over oven heating tests is that measurements can be carried out at temperatures similar to those found during e.g. self-heating in silos and stockpiles, thus eliminating the need for extrapolation. Interpretation of isothermal calorimetry data however also requires the assumption of a reaction model. A common model is to split the observed heating rates into an oxygen-dependent and an oxygen-independent reaction, and to assume the rates follow an Arrhenius expression [81, 82].

2.4. Characteristics of biomass

From the above review of self-ignition theory and experimental literature data, two aspects stand out: the fact that self-heating and self-ignition are described by a highly simplified reaction model, and that self-heating and self-ignition properties are highly material dependent. This suggests to examine the characteristics of biomass further with respect to self-heating. In the first part of this section, material properties of biomass are briefly reviewed, showing that biomass is a highly inhomogeneous material. In the second part, (qualitative) mechanisms are reviewed, that explain reaction initiation and propagation in biomass based on its structural characteristics.

2.4.1. Structural properties of biomass

Although biomasses differ among each other quite widely depending on origin, they have some characteristics in common which distinguish them from fossil fuels. Raw biomass is characterized by a higher moisture, higher volatile, and a lower ash content as compared to solid fossil fuels [84]. A higher moisture content means that more water has to driven off before or during combustion, which acts as a heat sink. Some of this water may also be removed through pre-treatment processes. Fuels with a higher volatile content are generally easier to ignite.

Generally, biomass has a higher H/C and O/C ratio than coal [1, 84]. The elemental composition is closely linked other combustion-relevant properties, such as the calorific value, the flammability limits and the ignition temper-
nature. Biomass also has different ash properties from coal, most notably a higher potassium content [84].

Biomasses from similar origin tend to have similar physical and chemical properties. Within the group of terrestrial plants, subgroups can be formed based on the type of plant, e.g. woods, grasses and straws [84]. Further distinctions may be made by differentiating between e.g. soft- and hardwood; or between different parts of the plant, such as stemwood, bark, and leaves or needles. Plant biomass is composed mainly of cellulose, hemicellulose and lignin. These materials form the plant cell walls [85], and are summarily referred to as lignocellulose. Cellulose is bound to lignin and hemicellulose by hydrogen bonds, while lignin and hemicellulose are also chemically bound [85].

Of these biomass components, cellulose is the most uniform. It is a linear polymer of glucose-units [85]. The pyrolysis kinetics of cellulose are largely independent of degree of polymerization and crystallinitiy, but are highly sensitive to ash content [86].

Hemicellulose is a general term for a number of polysaccharides which differ from plant species to plant species [85, 87, 88]. Xylans are the dominating hemicellulose in hardwood, but nearly all species contain at least some amount of xylans [85]. This may be a reason why xylan is by far the most common hemicellulose-substitute in studies of ‘pure’ components, as suggested by [89]. However, the thermal behavior of hemicelluloses differs quite substantially [88, 90–92]. Especially xylan is somewhat unusual compared to other hemicelluloses: It is thermally less stable and its decomposition in inert atmosphere is exothermal, whereas other hemicelluloses decompose endothermally (if secondary reactions are inhibited) [91]. Moreover, xylans in terrestial plants mainly occur as heteropolymers, i.e. branched with other sugars. Common heteroxylans are glucuronoxylans in hardwoods or arabinoxylans in cereal grains [87]. Glucuronoxylan was not investigated in [91], but arabinoxylan showed a starkly different behavior from xylan in that study, appearing much more thermally stable in thermogravimetric analysis. Softwood-hemicellulose is mainly based on glucomannans and galactoglucomannans [87]. Glucomannans have a reactivity lower than xylan and higher than arabinoxylan [91, 93]. From experiments with glucomannanns of different origin, it is thought that the ratio of glucose to mannose has an influence on its decomposition behavior [93]. This complexity of hemicellulose may be the reason why even very detailed reaction schemes considering “hemicellulose” [92, 94, 95] yield only somewhat imperfect predictions of pyrolytic mass loss.

Lignin is a amorphous, three-dimensional biopolymer based on aromatic groups.
Lignin is difficult to extract without altering its structure, which is why a series of lignin models exist [85]. Native lignins differ structurally depending on plant species, and isolated lignins additionally differ depending on the isolation process [85, 88, 90, 96]. The basic building blocks of lignin are syringyl lignin, guaiacyl lignin and hydroxyphenyl lignin. Hardwood lignins contain high amounts of syringyl and some guaiacyl, softwoods and other gymnosperms contain mainly guaiacyl [85, 88]. Ranzi et al. [94] suggested the use of carbon-rich, hydrogen-rich, and oxygen-rich lignin as model compounds in biomass pyrolysis. These pseudo-species are however not directly mapped to syringyl, guaiacyl and hydroxyphenyl lignins.

Extractives are other organic components present in plants, without structural functions. These include lipids, resins, tannins, and other sugars. Extractives can be removed from the plant cell matrix by washing in either polar or non-polar solvents. Their thermal decomposition may generally occur in the same range as that of cellulose, hemicellulose and lignin [88, 97]. However, it has been observed that the decomposition of biomass naturally poor in extractives [98] or extracted biomass begins at higher temperatures than that of unextracted biomass [88, 89]. The process of extraction is however also thought to alter the hemicellulose structure [90].

Shafizadeh and McGinnis [99] suggested that thermal decomposition (pyrolysis) of biomass can be described as the sum of its components’ behavior. Component-based kinetic models can now be considered state-of-the art to model pyrolysis reactions of biomass (as reviewed e.g. in [88, 100, 101]). Unlike proposed in [99], most models are however not based on superimposing the kinetics of isolated cellulose, hemicellulose and lignin components. This is due to non-negligible interactions among the components, catalyzing effects of ash-forming metals, and structural changes caused when isolating the components [88, 100]. Component-based models therefore are based on describing the apparent behavior of components as they appear in natural biomasses.

### 2.4.2. Reaction initiation in biomass

Self-heating in biomass can be initiated by microbiological activity [102–106], chemical oxidation [103, 105, 107, 108], and adsorption of moisture [104, 105, 107, 109]. Mechanisms of wood degradation were reviewed by Krigstin and Wetzel [103]: Metabolism of thermotolerant bacteria and thermophilic fungi were reported in several studies as heat sources in stored wood piles. Temperatures in stockpiles could typically increase up to 333 K. Biological activity was however rarely reported above these temperatures. Bacterial colo-
CHAPTER 2

Pulverized-coal fired power plants are converted to biomass firing in Denmark. Some adaptations have to be made to plants and operating conditions. Among others, the temperature of combustion air has to be lowered. The air is used to transport particles from mill to burners, and pre-heating this air stream is a method to internally recycle heat. However, excessive air temperatures are seen as a major cause for mill fires. At present, there is insufficient data available to reliably predict initiation and progression of mill fires. Mill operation temperatures for combined heat and power plants running on wood pellets may therefore be unnecessarily low, entailing a loss.
of fuel efficiency.

As outlined above, super-critical self-heating leading to self-ignition likely plays a key role in mill fires. Determining self-ignition propensity is currently based on extensive lab-scale testing. Scaling of these data to conditions relevant to industrial applications frequently relies on very simple models, that often neglect the complex structure of biomass. Additionally, data reported by different researchers shows considerable scatter. Only few conclusions can therefore be drawn by aggregating such datasets, and they offer little in terms of understanding the mechanism of self-heating. On the other hand, a large body of more qualitative works is available, seeking a mechanistic understanding of biomass degradation and oxidation. Combining these two lines of research may offer new insights into biomass self-heating and self-ignition in power plants.

The program for this work is therefore to attempt an answer to the following:

• Can the role of low-temperature oxidation be confirmed?
• Can a reaction kinetic model be determined at temperatures relevant to self-heating and self-ignition in mills?
• Can such a mechanism be validated and used in modelling self-heating and thermal runaway?
• Can the tendency to ignite be traced to differences in composition between biomasses?
3. Flaming, glowing and mild charring - an experimental study on oxidative reactions of wood

3.1. Introduction

Fires in mills, but also in storage facilities, are a threat to the safe and reliable operation of power plants with biomass as a fuel. There is some evidence to suggest that mill fires start from smoldering accumulations of settled particles [12, 28, 30, 31, 33, 34, 112], although this has not been extensively researched. The aim of this study is to gain some qualitative insights on low-temperature oxidation of biomass, especially wood particles, which can then be used to develop models for the onset of mill fires.

Combustion is commonly thought of as a sequential process of particle drying, devolatilization, homogeneous oxidation of the volatiles followed by heterogeneous oxidation of the char. Howard and Essenhigh [113] found that a heterogeneous reaction at the particle surface may occur parallel to devolatilization. In their study, pulverized coal of a known size distribution underwent the stages of a brief period of volatile release, followed by a heterogeneous ignition of the particle surface, which then continued oxidizing and devolatilizing at the same time. A further analysis concluded that there was a critical particle radius, above which an increased volatile flux from the surface would screen the surface from oxygen contact, thus pushing the reaction zone further outward. Similar findings are reported by Saastamoinen et al. [114], whose analysis included the effect of particle temperature and oxygen content. From experiments with coal and peat and model calculations, they concluded that the successive devolatilization-char-combustion-mechanism is not relevant below 1373 K. Further research was aimed at the influence of temperature and particle size [114–117], heating rates [116], the application to packed beds [117, 118] and dust clouds [115, 116]. It was found that small particles [113, 115], higher oxygen concentration [115], low temperatures [114, 116] and high heating rates [116] favor a direct oxidation of the unpyrolyzed particle. However, the various factors have a high interdependency [113–117], and combustion mode may even switch back and forth,
as a heterogeneous reaction on the particle surface releases more volatiles, favoring homogeneous volatile combustion [113, 118].

Ignition properties of biomass have been investigated under conditions resembling pulverized fuel fired boilers [119] and packed bed or grate firing systems [117, 118], as well as for smoldering containers of pellets [120]. This work deals with the temperature range in between, that is lower than that in firing systems but higher than the temperatures reached in storages.

3.2. Experimental

Pine wood was used in the majority of experiments presented. The sample material had been milled and sieved into fractions, of which the size range 600–1000 µm was used. Other experiments were carried out on a finer fraction of the same pine wood (50–200 µm), milled beech wood and a sample of commercial sunflower husk pellets. Information on the composition from ultimate and proximate analysis is summarized in Table 3.1. Further experiments were carried out with commercially acquired cellulose, lignin and xylan (Sigma-Aldrich C6288, Sigma-Aldrich 471003 and abcr Chemie AB143294). All pulverized samples were pressed into pellets to allow easier handling. The pellets had a diameter of 10 mm and a height of approximately 3.5–4.5 mm. Pellets had a mass of approximately 0.25–0.27 g each. The densities of the pellets fall within a range of 700–980 kg m⁻³, which is above the density of raw softwoods (≈400–600 kg m⁻³) and at the upper end of hardwood densities (≈600–900 kg m⁻³) found in the literature [19]. The pellets can therefore be expected to behave like solid, isotropic particles. A series of heavier pine wood pellets were produced to assess the influence of pellet mass variations. The sunflower husk pellets were broken into smaller pieces, but otherwise used as delivered. All materials were tested as-is, i.e. without pre-drying.

A single particle reactor with optical access was used in the experiments, Fig. 3.1. The main part of the reactor is a glass tube of ca. 5 cm inner diameter, which is externally heated by electrical resistance heaters. At around

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>volatiles</th>
<th>char</th>
<th>ash</th>
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<td>0.027</td>
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<td>0.141</td>
<td>0.003</td>
</tr>
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<td>0.059</td>
<td>0.503</td>
<td>0.015</td>
<td>0.756</td>
<td>0.193</td>
<td>0.052</td>
</tr>
</tbody>
</table>
2/3 of the height, the reactor has four access ports oriented at right angles. One of these is used to insert samples horizontally. The other ports are used for optical access or remain unused. Samples were placed on a small glass crucible, which was suspended from a glass sample holder. A thin (0.5 mm) type K thermocouple was positioned under the sample in the crucible. Sample and crucible could be kept in a retracted position outside the heating zone and flushed with nitrogen. At the beginning of the experiment (t = 0 s), the sample was rapidly inserted into the center of the reactor. Oven temperatures are controlled via a thermocouple on the outside of the reactor. The controller had previously been calibrated to known temperatures inside the oven, using well-defined salt melting points. This calibration had previously been carried out at temperatures above 1073 K, i.e. above the temperature range investigated here. Oven temperatures reported in this work are setpoint (wall) temperatures. To determine the temperature seen by the particle, a calibration curve was measured which related the temperature measured in an empty crucible to the oven temperature.

A continuous flow through the reactor allows controlling the atmosphere inside the reactor. The total flow rate was 1 L min⁻¹ at standard conditions for all experiments. Oxygen and nitrogen were mixed to a global oxygen concentration of 25% inside the reactor. The bulk part of the flow (0.47 L min⁻¹) enters the reactor at the bottom, with additional purge gas streams entering at the ports. The purge gas streams at the sample insertion port and the one opposing it were nitrogen only. The sample was therefore kept in nearly inert atmosphere at the start of the experiment.
For a small subset of experiments, water was added to the atmosphere inside the oven. A syringe pump of type Braun perfusor compact S was used to feed 3 mL h\(^{-1}\), 6 mL h\(^{-1}\) and 12 mL h\(^{-1}\) water, respectively, to a steam generator. Experiments were carried out at 533 K oven temperature. At this temperature and ambient pressure, the added vapor amounts correspond to 0.12 L min\(^{-1}\), 0.24 L min\(^{-1}\) and 0.49 L min\(^{-1}\), respectively. The steam generator outlet was attached to the bottom inlet of the reactor. Tubes connecting steam generator and reactor were heated to 413 K to avoid condensation. The experiments with added humidity were carried out on pine samples.

During the experiment, the thermocouple signal was constantly recorded, giving the approximate temperature of the sample. In the off-gasses, oxygen concentration was monitored in range 0–27\%\, carbon monoxide (CO) and carbon dioxide (CO\(_2\)) in range 0–10\%, and additionally CO\(_2\) in range 0–3000 ppm. The analyzers were placed in series: the flow first passed through an ABB-analyzer for CO and CO\(_2\) (high) and after that through an Emerson NGA 2000 analyzer for O\(_2\) and CO\(_2\) (ppm). All data was recorded in 0.5 second intervals.

From the free viewport, images were recorded with a Nikon D90 digital camera with a 50 mm/f1.8 Nikkor lens. Apertures were manually set within a range of f4–f5.6, and the shutter speed adapted to the available light. The camera was mounted on a tripod during the experiments.

### 3.3. Results

#### 3.3.1. Reaction regimes

Three distinct regimes could be identified in the experiments: a mild charring with slight discoloration of the sample and little mass loss, a glowing mode of oxidation, and a flaming combustion. The behavior of the sample depended on the oven temperature, Table 3.2. Both flaming and glowing modes led to a complete burnout and left only a small residue of (mainly) ash. For beech, pine and sunflower husk pellets, a threshold temperature was seen between mild reaction and glowing ignition. For cellulose, lignin and xylan, this distinction was less clear. As will be discussed further below, those samples showed a behavior that differed from both woods and the sunflower husks.

Regardless of material, none of the samples that started glowing at \(\leq 573\, \text{K}\) would spontaneously start flaming. Therefore, experiments were carried out with pine pellets at higher temperature to establish when flaming would occur. Control experiments with pine wood pellets of higher mass (≈0.4 g, 0.6 g)
showed that the threshold for onset of glowing reactions is slightly lowered as mass is increased (no ignition at 513 K, ignition at 523 K oven temperature for both types of heavier pellets). Comparison of experiments with pellets made from the finer pine wood fraction (50–200 µm) in a range of oven temperatures between 533–723 K showed no appreciable difference to the pellets made out of coarser wood particles. Effects of sample mass and original particle size were therefore neglected in the following.

From the time-temperature history of the pine experiments (Figure 3.2), the difference between the mild reaction regime and the glowing mode is especially obvious. At a setpoint of 523 K, only mild self-heating is observed, while a sample pellet exposed to 533 K will undergo self-ignition, as seen by the large temperature overshoot (ΔT ≈ 300 K). There is a delay between inserting the sample (at t = 0 s) and the sharp increase in temperature at ignition. During this period, heating of the sample changes from external heating to self-heating. Increasing the temperature that the pellet is exposed to shortens this ignition delay time from 300–400 s at 533 K to a time in the order of few tens of seconds. In some cases, pre-heating of the pellet in the retracted position could not be avoided, as seen by the temperature for time <0 s. Nevertheless, all curves show a characteristic dent for t >0 s, indicating the transition from (external) heating to self-heating and eventual thermal runaway. At higher reactor temperatures, the maximum temperature attained during burnout increases, and the time for burnout decreases. For cases 713 K and 723 K, flaming was observed, while glowing of the solid sample occurred for 533–703 K.

Table 3.2.: Ignition/non ignition for different materials. ○= mild or no reaction, ●= smoldering/glowing, ▲= flaming, –= not tested. (xylan): no temperature overshoot, but significant release of CO and CO₂, (lignin): temperature overshoot, but no visible glow

<table>
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<tr>
<th>oven temperature wall [K]</th>
<th>crucible [K]</th>
<th>beech</th>
<th>pine</th>
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<th>xylan</th>
<th>cellulose</th>
<th>lignin</th>
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Flaming, glowing and mild charring

Figure 3.2.: Time-temperature history of the pine experiments by oven setpoint temperature. Critical cases are highlighted, where 533 K: lowest oven temperature for which glowing was observed, 703 K: highest oven temperature for which glowing was observed, 713 K: lowest temperature for which flaming was observed. Compare Table 3.2.

The off-gas concentrations of CO and CO$_2$ corresponding to the temperature measurements are seen in Figures 3.3 and 3.4, respectively. In agreement with the time-temperature histories, release of CO and CO$_2$ occurs earlier and with higher intensity for higher ambient oven temperatures in the case of glowing oxidation (533–703 K). For flaming combustion, a large overshoot in CO$_2$ is observed. CO is only detected in relevant amounts in the flaming experiments (713 K, 723 K) up to the ignition of the volatiles and during the char burnout phase, but not while the flame is present. Owing to their different behaviors, glowing and flaming are interpreted as distinct mechanisms, where glowing is seen as a heterogeneous oxidation of the solid and flaming as a two-step process of devolatilization and homogeneous oxidation in the gas phase.

3.3.2. Characteristics of the glowing regime

Figure 3.5 illustrates glowing ignition and burnout for a pine sample at 533 K oven setpoint temperature. Qualitatively, it is observed that the pellet first
Figure 3.3.: Time-CO history of the pine experiments by oven setpoint temperature

Figure 3.4.: Time-CO₂ history of the pine experiments by oven setpoint temperature
Flaming, glowing and mild charring

Figure 3.5.: Glowing ignition and burnout of a pine wood pellet. See text for discussion.
expands slightly—possibly due to evaporation of moisture or release of gases, which push the dust or grains apart. At around 300 s, the particle has visibly darkened and reached a temperature of 550 K. Discoloration of wood is associated with degradation of hemicelluloses \[121\]. At 400 s and 600 K, the particle has lost in volume and appears black in color. A considerable amount of blur is visible in the images. The likely source is fumes (organic volatiles and water vapor) released from the reacting particle. Off-gas concentrations of CO and CO\(_2\) reach 0.16\% and 0.32\% at this point, respectively. A visible glow appears on the top left corner of the particle in the frame at 429 s, which then spreads throughout the particle. Temperatures rapidly increase at this point. Glowing is likely due to blackbody radiation. Empirically, \(\approx 798\) K has been determined as a threshold temperature at which blackbody radiation gradually becomes visible to the human eye \[122\]. Since the surroundings are well-lit, temperatures are likely much higher when glowing appears in the images. Fumes gradually disappear, while the particle continues to burn out completely. The recovered residue was 2 mg of the original 268 mg.

From the measured mole fractions \(y\) of CO and CO\(_2\), the amount of carbon released in the form of both gases can be calculated:

\[
m_{C,i} = M_C \cdot \int \left( y_i \cdot \dot{V}_{gas, STP} \right) dt \cdot \frac{P_{STP}}{R \cdot T_{STP}};
\]

\(i = \text{CO, CO}_2\) \hspace{1cm} (3.1)

where \(M_C\) is the molar mass of carbon, \(\dot{V}_{gas, STP}\) the volumetric flow rate at standard temperature and pressure (STP), and the fraction \(p_{STP}/(R \cdot T_{STP})\) the conversion factor between volume and molar quantity for ideal gases at STP. The total amount of carbon as CO and CO\(_2\) can then be compared to the amount initially present in the sample, based on the initial sample mass \(m_0\), the carbon fraction of 53\% (Table 3.1) and an assumed moisture of 5\% by mass. Results are summarized in Table 3.3.

Table 3.3.: CO and CO\(_2\) released from pine pellets at different oven temperatures

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<tr>
<th>wall temperature [K]</th>
<th>crucible temperature [K]</th>
<th>(m_0) [mg]</th>
<th>(m_C) as CO [mg]</th>
<th>(m_C) as CO(_2) [mg]</th>
<th>(m_C) as CO [%]</th>
<th>(m_C) as CO(_2) [%]</th>
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</table>

36
For increasing reactor temperatures in glowing combustion mode (temperature range 533–703 K), the samples are seen to produce slightly more CO at higher ambient temperature, while the amount of fuel carbon converted to CO₂ stays roughly constant (34%). CO to CO₂ ratios increase from 0.4 to 0.5 within the glowing regime. In total, only 46–52% of fuel carbon was found in CO and CO₂ for the glowing experiments, indicating that significant amounts of carbon must have been released in the form of other species (likely hydrocarbons). This would qualitatively agree with the fumes or volatile clouds visually observed in the reactor as well as with condensed tars found on the filters of the analysis gas conditioning unit.

Results were qualitatively similar for beech and sunflower husk pellets, where the range 403–423 K was considered. A fraction of 53% of the fuel carbon was found in CO and CO₂ for beech when glowing ignition occurred, compared to 3.4% for the non-ignition case. The corresponding figures for sunflower husks are 56% and 5.9%, respectively. CO/CO₂-ratios during glowing oxidation are 0.3 for beech and 0.5 for sunflower husks. These results are similar to those of Grotkjær et al. [118], who report CO/CO₂ ≈0.15–0.5 using a similar experimental technique (pulse ignition).

The observations, especially in the larger range considered for pine, indicate that the overall conversion of the pellets proceeds in a qualitatively similar manner throughout the glowing regime. The ambient temperature only influences how rapid the conversion proceeds.

Data have been published on combustion efficiency of wood pellets [123, 124]. These can be compared to, and supplement, the measured values presented here. Sampling at quasi-steady burning conditions, Perzon [123] reports 2540 mg m⁻³ of CO and CO₂ and 3000 mg m⁻³ organic compounds for smoldering of softwood pellets. The majority of hydrocarbons during smoldering are methoxyphenols associated with decomposition of lignin, a second large group are furfural-related compounds [123]. Of the latter, 5-hydroxymethyl-2-furaldehyde is formed from hexoses, and 2-furaldehyde from pentoses [125], i.e. these compounds likely originate from decomposition of hemicelluloses (compare [126]).

With a similar measurement technique as in [123], Olsson et al. [124] find 4800 mg m⁻³ combined CO and CO₂, compared to 11 mg m⁻³ methane and 85 mg m⁻³ for C₂–C₇ hydrocarbons (ethane, ethene, ethyne, propene, 1,3-butadiene, furan, benzene, methylbenzene), also for softwood pellets. Under pyrolyzing conditions, Chen et al. [127] report peak release rates of 22% tar (by weight), compared to 2% CO₂, 1.2% CO and 0.12% methane from TG-FTIR experiments with a hardwood sample. While the type of data reported differs somewhat (mass versus volume concentrations, integral versus mo-
mentary data), some conclusions can be drawn: The glowing reaction regime is characterized by an incomplete oxidation of fuel carbon. CO and CO$_2$ appear mainly as oxidation products, but there is also a non-negligible contribution from purely thermal decomposition (pyrolysis). Oxidation is accompanied by pyrolysis of similar magnitude (i.e., with similar reaction rates). About half of the carbon present forms organic compounds. By comparison with [123, 124, 127], most of the remaining carbon mass is likely found in aromatic compounds (phenolic and furan-based), some in methane, and less in linear hydrocarbons. The visibility of fumes indicates that these species condense from the bulk gas phase and form droplets or fog.

By comparison, for the mild decomposition at lower temperatures (523 K), less than 4% of the fuel carbon was found as CO and CO$_2$, while the pellet lost 24% of its mass during the experiment. Peak release rates of both gases coincided with a peak particle temperature of 529 K at ca. 400 s. The receding temperature and product gas concentrations indicated that conversion rates had decreased by the time the experiment was stopped at 1500 s. Carbon conversion to CO and CO$_2$ for the flaming experiments could not be calculated as the measured concentrations temporarily exceeded the analyzer measurement range (0-10%).

### 3.3.3. The glowing/flaming boundary

Comparison of the two experiments around the glowing/flaming boundary (703–713 K) suggests that an equally sharp boundary exists between these two regimes as between the non-ignition and glowing cases at lower temperatures. Figure 3.6 shows images from both experiments. Both pellets appear to undergo the same process up to around 75 s after sample insertion. While a flame then spontaneously ignites and stabilizes around the pellet for 713 K oven temperature, the pellet in the 703 K-experiment continues to release volatile matter and eventually starts glowing. Although the pellet reaches temperatures of up to 950 K, it does not act as an ignition source to the volatiles, and these are eventually dispersed. By comparison, auto-ignition temperatures of methane is 868 K, and other alkanes have even lower auto-ignition temperatures [45]. Ignition temperatures for some furfural-derived compounds are reported within 543–686 K [128].

When flaming ignition occurred, it was accompanied by a sudden increase in pressure in the reactor. The pressure rise, while not measured or recorded, was sufficient to dislodge one or several of the loosely fitted viewing port glasses. In some cases, a very localized glowing ignition could be seen immediately before the onset of flaming. Similar observations have also been
Figure 3.6.: Spontaneous onset of glowing at 703 K (top 3 rows) and spontaneous onset of flaming at 713 K reactor temperature (bottom). No transition between regimes is observed.
reported by other researchers [119]. Based on the absence of transition between glowing and flaming, these may however be considered as independent, parallel processes. The onset of flaming, i.e. volatile ignition, is possibly governed by the homogeneous gas phase chemistry. It appears safe to conclude that volatile ignition (in the bulk gas phase) is not necessary to completely react the solid. Likely, it does not play a role for the onset of self-ignition.

### 3.3.4. Humidity

Experiments with added humidity in the gas phase were carried out at the lower threshold for glowing ignition of pine, 533 K. Glowing ignition and burnout was observed for all experiments, Figure 3.7. In two cases, the sample ignited several seconds earlier than in the dry case, in two experiments ignition was slightly delayed. Comparing the two experiments under the same nominal conditions (6 mL h\(^{-1}\) liquid added), this delay is possibly not significant. In one experiment (6 mL h\(^{-1}\) (2)), the sample extinguished and re-ignited at around 500 s. This could be seen both visually (glowing–dark–glowing) as well as in a sharp drop in sample temperature (Fig. 3.7), and in CO and CO\(_2\) emissions, which then rebounded. Fuel car-

![Figure 3.7.: Time-temperature history of pine pellets exposed to 533 K oven setpoint temperature with humidity added in the gas phase](image)
bon conversion to CO and CO$_2$ did not appear to be influenced by the addition of water (Table 3.4). No clear trend could be established from adding (large) amounts of water vapor to the gas phase at 533 K. Biomass samples are themselves a source of water vapor, both via evaporation of water bound in the particles, as well as by conversion of fuel hydrogen (both oxidative and pyrolytic). Whether the added water interacts with these mechanisms or whether additional effects, such as gasification reactions of water vapor or changes in thermal properties of the bulk gas phase (thermal conductivity, density, specific heat capacity) play a role could not be clarified within the scope of this work.

### 3.3.5. Cellulose, Lignin and Xylan

Experiments on the commercial cellulose, lignin and xylan samples are summarized in Figures 3.8 through 3.10. All experiments were carried out at 573 K oven setpoint temperature. All samples visibly charred, but only cellulose showed a weak glow during the experiments. Absence of glowing can be explained by low peak temperatures.

The time-temperature profile of the cellulose sample resembles that of pine most closely (compare Fig. 3.2). Lignin shows a short phase of overheating, with a comparatively low temperature overshoot. The xylan sample did not show any signs of self-heating. Instead, the sample appeared to soften, ‘melt’, bubble and eventually turn into a highly porous char, that had a volume several times higher than the original pellet. At the end of the melting phase, the sample gradually changed color from white to yellowish, then to red-brown, and finally turn black. Discoloration, but not softening, was also observed for cellulose. Images for both xylan and cellulose pellet can be found in Appendix A.1. The color change can be associated with pyrolytic breakdown of carbohydrates [125].

<table>
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<th>liquid [g h$^{-1}$]</th>
<th>vapor [L min$^{-1}$]</th>
<th>$m_0$ [mg]</th>
<th>$m_{c\text{ as CO}}$ [mg]</th>
<th>$m_{c\text{ as CO}_2}$ [mg]</th>
<th>$m_{c\text{ as CO}}$ [%]</th>
<th>$m_{c\text{ as CO}_2}$ [%]</th>
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<td>13.9</td>
<td>35.5</td>
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Table 3.4.: Influence of humidity on CO and CO$_2$ released from pine pellets at 533 K oven temperature. Vapor is the volumetric flow rate at 533 K, calculated from the amount of liquid water added.
Figure 3.8.: Time-temperature history of xylan, lignin and cellulose pellets exposed to 573 K oven setpoint temperature. The sudden drop in sample temperature at the end of each experiment is due to quenching when retracting sample holder, crucible and thermocouple.

For the release of CO and CO$_2$, cellulose was the only material tested for which emissions of CO were higher than those of CO$_2$ (Figures 3.9 and 3.10). A relatively large fraction of the sample mass was recovered after the experiment, especially for lignin (Table 3.5). For cellulose, lignin and xylan, only 91\%, 37\% and 71\% of the initial mass were lost, where the corresponding figures for beech, pine and sunflower are 99\%, 99\% and 97\%, respectively, for complete burnout.

Carbon contents of cellulose, lignin and xylan were estimated as 0.44 kg/kg, 0.63 kg/kg and 0.4 kg/kg, respectively, based on data found in the Phyllis2-database [129]. Conversion of fuel carbon to CO and CO$_2$ was calculated with these approximations, and are included in Table 3.5. Conversion of the cellulose, lignin and xylan samples to CO and CO$_2$ was much lower than for any other sample upon ignition (beech, pine, sunflower: 46–56\%). Slightly lower degradation rates of isolated components compared to native wood under pyrolyzing conditions (673–1273 K) are reported in [126]. In oxidizing environment and at the temperatures reached during conversion here (373–773 K), a similar effect is seen.
Figure 3.9.: Time-CO history of xylan, lignin and cellulose pellets exposed to 573 K oven setpoint temperature.

Figure 3.10.: Time-CO$_2$ history of xylan, lignin and cellulose pellets exposed to 573 K oven setpoint temperature.
3.4. Conclusions

A study on low-temperature oxidation (523–723 K) on different biomasses was carried out. Pine wood was used in the majority of experiments, with additional experiments on beech wood, sunflower husk pellets, as well as cellulose, lignin and xylan powders. Three oxidative reaction regimes could be identified: a slow decomposition involving mild self-heating, a glowing ignition and a spontaneous flaming ignition. Glowing ignition is interpreted as a heterogeneous oxidation of the solid, where the visible glow is blackbody radiation of the sample. Flaming is a homogeneous oxidation of volatiles in the gas phase around the particle. Both oxidation regimes lead to complete burnout of the sample. In experiments carried out on pine wood pellets of ≈250 mg, glowing reactions occurred for ambient temperatures within a relatively broad temperature range of 533–703 K. Although glowing samples exceeded the critical ambient temperature for flaming, no transition between the two modes was seen.

During glowing combustion, carbon conversion to CO and CO$_2$ is highly incomplete. Integrated over the duration of the experiment, approximately 33–35% of carbon mass was found in CO$_2$, and another 12–18% in CO. By comparison with literature data, a large fraction of the remaining carbon mass is likely found in aromatic compounds. This qualitatively agrees with the fumes observed in the experiments.

The isolated components cellulose, lignin and xylan (used as a hemicellulose representative) behaved differently from native, (whole) biomasses in the experiments. Residual masses were higher and conversion to CO and CO$_2$ much lower than those observed for the wood and sunflower husk samples under similar conditions. Degradation of xylan also visually differed from that of all other samples. In this study, behavior of biomasses could not be explained as the sum of the behavior of its components.

In conclusion, heterogeneous oxidation and pyrolysis appeared as the dominating mechanisms in low-temperature reactions of biomass. Self-heating leading to ignition could be observed from ≈523 K upwards. The amount of
carbon found in CO and CO$_2$ suggests that pyrolysis and oxidation rates have similar magnitudes. Modelling self-heating and self-ignition should therefore include (at least) these two reaction pathways.

### 3.5. Symbols and abbreviations

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<th>Base units</th>
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<td>kg mol$^{-1}$</td>
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<tr>
<td>$m$</td>
<td>mass</td>
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</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
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<td>K</td>
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<tr>
<td>$y$</td>
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<table>
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<td>g</td>
<td>gas</td>
</tr>
<tr>
<td>i</td>
<td>index for species</td>
</tr>
<tr>
<td>STP</td>
<td>at standard temperature and pressure</td>
</tr>
<tr>
<td>tot</td>
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</table>
4. Kinetic parameters for biomass at self-ignition conditions - low temperature oxidation and pyrolysis

A version of this chapter has been published by Energy & Fuels.1

4.1. Introduction

Biomass can replace coal as a fuel for heat and power generation in pulverized fuel fired boilers. One recent example is the conversion of Danish combined heat and power (CHP) plants originally built as pulverized-coal fired boilers. This technological switch requires to store and process solid biomass materials, mainly in form of pellets, in large quantities. In CHP-facilities, fires have occurred in storages and power plant mills that were likely caused by spontaneous ignition. Excessive self-heating, leading to thermal decomposition and ignition, is a known problem for storages [82,108]. To the authors’ knowledge, the role of self-ignition of biomass in mill fires, i.e. at elevated temperatures above 423 K, has not been explicitly researched. However, based on older studies of coal mills, settled dust beds may build up and self-ignite in these devices [30,33,34]. Predicting such events requires accurate reaction kinetic data for low temperatures. Unfortunately, such data are scarce for typical fuels such as wood pellets and agricultural residues.

Additionally, there does not appear to be a consensus on the appropriate kinetic model for low temperature oxidative conversion. Different researchers have proposed single-reaction models [73,77,81,82,130,131], models with two or more parallel reactions [111,132-137], models with two or more sequential reactions [138-140], and models involving combinations of serial and parallel reactions [141-146]. Where several reactions are used, these have been used to distinguish between pyrolysis and oxidation, between different biomass components, or different stages of pyrolysis and/or oxidation reaction pathways. A short overview will be given below in the light of deter-

mining kinetic parameters at temperatures relevant to self-heating in power plant mills.

If only a single reaction is used to model low temperature oxidation, the reported kinetic parameters vary widely. Activation energies for wood pellets from isothermal calorimetry at low temperatures (300–350 K) have been measured as 50–80 kJ mol\(^{-1}\) [81, 82]. From oven heating tests, 89 kJ mol\(^{-1}\) are reported for mahogany wood at 375–450 K [111]. Data compiled from oven tests of different wood species at 370–570 K result in activation energies of 110–125 kJ mol\(^{-1}\) [130].

From self-ignition oven tests according to EN15188, activation energies of 139 kJ mol\(^{-1}\) and 207 kJ mol\(^{-1}\) are reported for sunflower husk pellets and softwood chips, respectively [77]. Kinetic parameters from tests on larger samples may also be influenced by heat and mass transfer limitations. Thermogravimetric analysis (TGA) is considered a method to avoid such transport limitations. Single-reaction models have been fit to TGA data, and activation energies for oxidation of forestry and agricultural residues are given in the range of 61–68 kJ mol\(^{-1}\) (at 293–1073 K) [73] and 75–116 kJ mol\(^{-1}\) (at 500–630 K) [131].

Thermogravimetric analysis has also been used to determine reaction kinetic parameters for biomass oxidation and pyrolysis in more complex models [132–140, 142–146]. The most widespread method is to conduct experiments at several constant heating rates from ambient conditions to temperatures exceeding 873 K or higher. The experimental data are in turn used to fit the parameters of a reaction model consisting of two or more sequential or parallel reactions, so that this best matches the conversion rate \(dX/dt\) as a function of temperature. Mass loss at low temperatures (<470–525 K) is frequently very low, however, and not well resolved in the reported experimental data. In the few cases in which mass loss is reported at these temperatures, it is attributed to evaporation of moisture [145, 146]. In both of those cited works, the evaporation peak is also clearly offset from oxidation and/or pyrolysis of the organic fraction when plotting conversion rate over temperature. Significant thermal or oxidative degradation below 470 K is not described in any of the cited TGA-studies [132–140, 142–146]. Comparison with the experiments at low temperatures (370–570 K) and long holding times (minutes to years) [81, 82, 111, 130], where significant conversion of the organic fraction is observed, suggests that the heating rates used in typical TGA-studies are too high to resolve the slow reactions at low temperatures. While experimental procedures slightly vary among researchers [132–140, 142–146], the lower bound for heating rates is usually 5–10 K min\(^{-1}\) (Anca-Couce et al. [134] also investigated 2.5 K min\(^{-1}\)), with an upper bound of typically
20–40 K min$^{-1}$. Such heating rates are interesting to describe propagation of smoldering combustion, which is associated with heating rates in order of 10–1000 K min$^{-1}$ [141]. In contrast, this work focuses on the initiation and onset of smoldering. Based on practical experience with ignition in mill fires, it is suspected that this incipient smoldering occurs on much larger timescales and at lower temperatures. Isothermal [147–150] and stepwise isothermal thermogravimetric analysis [151, 152] have been used to investigate torrefaction reactions (a mild pyrolysis, $\approx$473–573 K), while only few comparable works are available for oxidative atmosphere (e.g., [153]).

The aim of this work is to extend kinetic models of devolatilization and oxidation to lower temperatures and heating rates. We present a model to describe mass loss kinetics for six different biomasses, distinguishing between pyrolysis and heterogeneous oxidation as parallel processes. Thermogravimetric analysis with stepwise isothermal programs in the range of 423–523 K is used to find the values of the kinetic parameters for each of the biomasses investigated. The oxygen concentration is varied in the experiments (0%, 20% and 80% oxygen) to separate purely thermal decomposition (pyrolysis) from oxidative reactions, and to determine the influence of oxygen on the reaction rates. The kinetic models found for low temperatures under isothermal conditions are then compared to thermogravimetric experiments at intermediate heating rates (5 K min$^{-1}$) and temperature ranges 373–773 K to ensure that they are consistent with the data available in the literature for those conditions.

4.2. Experimental

Six different biomasses were investigated: beech wood, pine wood and wheat straw as raw materials, as well as two types of wood pellets obtained from a local CHP-plant, and a sample of sunflower husk pellets as commercial pelletized fuels. Additionally, experiments were carried out with cellulose (Sigma-Aldrich C6288), xylan (from cornstalk; abcr Chemie AB143294) and lignin (alkali; Sigma-Aldrich 471003). Rapeseed oil was used as a model substance for extractives, as it contains a mix of saturated and unsaturated fatty acids (mainly C18:1 and C18:2). Unsaturated fatty acids may play a role in the autooxidation of biomass [108]. In order to model extractives bound in a matrix, experiments were carried out with mixtures of oil and SiO$_2$ as well as oil and cellulose, both 50%/50% by weight.

The two woods were provided in pulverized form (beech: 0–250 µm, pine: 50–200 µm). The other biomass samples were milled and a size fraction <125 µm was used in the experiments. Cellulose, lignin and xylan were used
as provided by the manufacturer. Information on the chemical properties of the six biomass materials used is found in Table 4.1. Results from proximate and ultimate analysis fall within the range of values typically found in the literature, although pine and wood pellets appear to have low char and high volatile contents. Of the inorganic elements present in the samples, especially potassium and sodium are known to have a catalytic effect on thermal conversion [88, 100, 150, 154, 155]. Other metals observed to have catalytic effects are magnesium [150] and, to a lesser extent, calcium [154].

4.2.1. Biopolymer analysis

Klason lignin and carbohydrate composition of the six samples were determined by sulfuric acid hydrolysis. 1.5 mL of 72 % H₂SO₄ were added to 0.16 g sample, which was pre-hydrolyzed for 60 minutes at 303 K. After dilution of the hydrolyzate with Milli-Q purified water (42 mL), the liquid samples were autoclaved at 393 K for further 60 minutes. Filtered liquids were analyzed on an HPLC (high-pressure/high-performance liquid chromatography) column, while the solid residue was heated to 823 K to determine the lignin ash content. Results are summarized in Table 4.1. For the two wood pellet samples, analyses from an external lab were available. The results agreed with the ones presented here within ±0.01 kg/kg, with the exception of glucose (0.401 kg/kg and 0.395 kg/kg for wood pellets I1 and I2, respectively), which showed slightly larger deviations.

Acid methanolysis and GC-MS (gas chromatography – mass spectrometry) was applied to three of the biomass samples in order to separate and quantify their hemicellulose-bound glucose content. The method is described elsewhere in more detail [156]. The analysis was done in duplicate and results were repeatable within 10 % of the reported values. Data is included in Table 4.1, based on the total dry matter.

Extractives were measured following a procedure based on an NREL report, Determination of Extractives in Biomass (NREL/TP-510-42619). Lipids were extracted with ethanol (96 v/v%) in a Soxhlet extractor for 6 hours to measure the amount of total extractives. The extracts were then chemically modified with 1.25 M HCl in methanol to produce fatty acid methyl esters, so that the fatty acids become detectable for the GC-MS instrument. An Agilent 7890B gas chromatograph interfaced to an Agilent 5977B Mass Selective Detector was used in this part of the study. Samples of 1 µL were injected in split mode (1:20). The source and rod temperatures were 503 K and 423 K, respectively. The products were separated using two HP-5ms ultra inert columns (15 m, 0.25 mm, 0.25 µm coating). Separation of products was achieved using a
temperature program from 343–523 K at 10 K min\(^{-1}\). Results are included in Table 4.1, where the relative abundance of the C16:0–C22:0 fatty acids are given for each biomass. The fatty acid values given are proportions, and do not allow an absolute quantification.

### 4.2.2. Thermogravimetric analysis

Thermogravimetric measurements were carried out on a Netzsch STA 449-F1 Jupiter. The instrument was checked by repeating a round-robin study on cellulose pyrolysis [157], as well as repeating pyrolysis experiments on beech [98] and pine [98, 134] at a heating rate of 5 K min\(^{-1}\). Agreement between our data and the kinetic models presented in the literature [98, 134, 157] was good. It was also found that kinetics derived from TGA with 5 K min\(^{-1}\) heating rates does not predict low-temperature mass loss well (see supporting information).

The focus of this work is on low temperature kinetics. Therefore, a temperature program for the TGA experiments was designed to investigate the region 423–523 K. The program consisted of a series of six isothermal stages: 423 K, 443 K, 463 K, 483 K, 503 K and 523 K. Each isothermal condition was held for one hour, with heating rates of 10 K min\(^{-1}\) in between stages and up to the first isothermal holding point (compare the top part of Fig. 4.1). Temperatures measured at the sample crucible generally followed the preset temperature programs well. A mild excess in temperature was seen at the beginning of each isothermal interval, which was attributed to a controller overshoot. The measured temperature history was used in the analysis of the data.

The gas flow rate through the oven was 150 mL/ min, and experiments were run under 0%, 20% and 80% oxygen (balance: nitrogen). Experiments were duplicated in range 423–503 K. To compare kinetic parameters determined in this work to data available in the literature, additional experiments were carried out at a constant heating rate of 5 K min\(^{-1}\) from ambient to 773 K, both under inert atmosphere and with 10% and 20% oxygen each. These experiments were also duplicated.

Samples were placed in alumina cups of 7 mm diameter and 4 mm height, which were filled to less than a third of their height. For the 5 K min\(^{-1}\) temperature ramp experiments, the sample mass was kept below 5 mg to avoid mass- and heat transfer limitations. For the isothermal experiments, slightly higher sample masses of <10 mg were allowed in order to better resolve the low mass loss at low temperatures.

The biomass samples were used as-is, i.e. without prior drying. Evaporation
Table 4.1.: Proximate, elemental and compositional analysis of the biomasses used in this study. Difference to one in the sum of the compositional analysis is balance error.

<table>
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<tr>
<th></th>
<th>Beech wood</th>
<th>Pine wood</th>
<th>Sunflower husks</th>
<th>Wheat straw</th>
<th>Wood pellets I1</th>
<th>Wood pellets I2</th>
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<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td><strong>Inorganic elements (selection), dry base [mg kg(^{-1})]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>4600</td>
<td>900</td>
<td>2600</td>
<td>2300</td>
<td>2000</td>
<td>1400</td>
</tr>
<tr>
<td>K</td>
<td>4600</td>
<td>360</td>
<td>8000</td>
<td>7500</td>
<td>1200</td>
<td>640</td>
</tr>
<tr>
<td>Mg</td>
<td>830</td>
<td>130</td>
<td>1400</td>
<td>690</td>
<td>420</td>
<td>320</td>
</tr>
<tr>
<td>Na</td>
<td>280</td>
<td>71</td>
<td>10</td>
<td>260</td>
<td>33</td>
<td>94</td>
</tr>
<tr>
<td><strong>Compositional analysis, dry base [kg kg(^{-1})]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.005</td>
<td>0.015</td>
<td>0.022</td>
<td>0.032</td>
<td>0.010</td>
<td>0.014</td>
</tr>
<tr>
<td>Galactose</td>
<td>0.007</td>
<td>0.025</td>
<td>0.009</td>
<td>0.011</td>
<td>0.013</td>
<td>0.026</td>
</tr>
<tr>
<td>Mannose</td>
<td>0.015</td>
<td>0.117</td>
<td>0.006</td>
<td>0.005</td>
<td>0.046</td>
<td>0.106</td>
</tr>
<tr>
<td>Rhamnose</td>
<td>0.004</td>
<td>0.002</td>
<td>0.008</td>
<td>0.002</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>Xylose</td>
<td>0.168</td>
<td>0.055</td>
<td>0.174</td>
<td>0.271</td>
<td>0.134</td>
<td>0.074</td>
</tr>
<tr>
<td>Galacturonic acid</td>
<td>0.025</td>
<td>0.013</td>
<td>0.048</td>
<td>0.008</td>
<td>0.204</td>
<td>0.013</td>
</tr>
<tr>
<td>Glucuronic acid</td>
<td>0.001</td>
<td>0.001</td>
<td>0.006</td>
<td>0.004</td>
<td>0.001</td>
<td>–</td>
</tr>
<tr>
<td>Sum non-glucose sugars</td>
<td>0.225</td>
<td>0.228</td>
<td>0.273</td>
<td>0.333</td>
<td>0.231</td>
<td>0.235</td>
</tr>
<tr>
<td>Glucose (total)</td>
<td>0.337</td>
<td>0.440</td>
<td>0.270</td>
<td>0.424</td>
<td>0.423</td>
<td>0.431</td>
</tr>
<tr>
<td>Non-cellulose glucose</td>
<td>0.016</td>
<td>0.037</td>
<td>0.009</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Klasson lignin</td>
<td>0.346</td>
<td>0.278</td>
<td>0.316</td>
<td>0.208</td>
<td>0.273</td>
<td>0.316</td>
</tr>
<tr>
<td>Extractives</td>
<td>0.015</td>
<td>0.093</td>
<td>0.089</td>
<td>0.039</td>
<td>0.066</td>
<td>0.072</td>
</tr>
<tr>
<td>Sum (composition)</td>
<td>0.923</td>
<td>1.039</td>
<td>0.948</td>
<td>1.004</td>
<td>0.993</td>
<td>1.054</td>
</tr>
<tr>
<td>Lignin ash</td>
<td>0.009</td>
<td>0.002</td>
<td>0.006</td>
<td>0.014</td>
<td>0.006</td>
<td>0.004</td>
</tr>
<tr>
<td><strong>Fatty acids analysis, relative abundance [arbitrary units]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C16:0</td>
<td>0.255</td>
<td>0.045</td>
<td>0.101</td>
<td>0.332</td>
<td>0.200</td>
<td>0.158</td>
</tr>
<tr>
<td>C18:0</td>
<td>0.058</td>
<td>n.a.</td>
<td>0.084</td>
<td>0.052</td>
<td>0.038</td>
<td>0.046</td>
</tr>
<tr>
<td>C18:1</td>
<td>0.190</td>
<td>0.207</td>
<td>0.199</td>
<td>0.123</td>
<td>0.188</td>
<td>0.184</td>
</tr>
<tr>
<td>C18:2</td>
<td>0.082</td>
<td>0.020</td>
<td>0.231</td>
<td>0.045</td>
<td>0.186</td>
<td>0.025</td>
</tr>
<tr>
<td>C18:3</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.046</td>
<td>n.a.</td>
<td>0.038</td>
<td>n.a.</td>
</tr>
<tr>
<td>C20:0</td>
<td>0.039</td>
<td>n.a.</td>
<td>0.018</td>
<td>0.020</td>
<td>0.024</td>
<td>n.a.</td>
</tr>
<tr>
<td>C22:0</td>
<td>0.108</td>
<td>0.024</td>
<td>n.a.</td>
<td>0.036</td>
<td>0.034</td>
<td>n.a.</td>
</tr>
</tbody>
</table>
of moisture was clearly visible in the recorded data as a pronounced loss of mass (between 4–8% depending on the individual sample, with typical values around 5% of the total) within the first 10 minutes of the experiment. As evaporation of moisture and decomposition of the organic matter were easily distinguished, no dedicated drying period was included in the heating programs. The measured moisture content was used to rescale the data to dry values.

Data were automatically recorded in 0.05-minute intervals for isothermal experiments, and in 0.01-minute intervals at constant heating rate. The sampling rates follow the default settings of the instrument. Recorded mass loss data were corrected for buoyancy effects by subtracting a correction carried out on an empty crucible for each experimental program. A simple routine for pre-processing the data was developed and applied to all datasets. Mass loss data were rescaled to dry base for further treatment, and \( m_0 \) refers to the initial dry mass in the following. To determine the conversion \( X \),

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

(4.1)

the final mass \( m_f \) was set to the sum of char and ash (from proximate analysis) for pyrolysis experiments, and only ash for experiments under oxidative atmosphere. Ash and char contents are found in Table 4.1. Owing to noise on the measured signal, the conversion rates \( dX/dt \) were determined from smoothed data. Data were initially smoothed by calculating the moving average of \( X(t) \) with a filter width of 120 records. From these data, the conversion rate was calculated as the temporal gradient by central differences. The conversion rate was then filtered again by applying the same moving average filter.

Repeatability of the experiments was generally good. In order to compare duplicate runs, the root-mean-square (RMS) difference was used.

\[
\delta_{\varphi} = \sqrt{\frac{\sum (\varphi_1(t) - \varphi_2(t))^2}{N}}; \quad \varphi = \{m/m_0, dX/dt, T\}
\]  

(4.2)

In this equation, \( N \) is the total number of datapoints measured at time \( t \), and \( \varphi \) is a placeholder for the compared quantities: remaining mass scaled by initial mass, conversion rate and temperature. This difference can also be scaled to the range of \( \varphi \)-values by

\[
\delta_{S_{\varphi}} = \frac{\delta_{\varphi}}{\varphi_{\text{max}} - \varphi_{\text{min}}}
\]  

(4.3)

Root-mean-square differences, data range, and scaled differences were determined individually for each biomass sample in each temperature program.
In the following, only the maximum differences and scaled differences across all measurements are given. The temperature-time programs agreed within a difference of $\delta T = 0.35 \text{ K}$ for all experiments. The relative mass remaining $m/m_0$ was repeatable within 0.0094 (6.5% of the measured range) for the isothermal experiments and 0.015 (1.8% of the measured range) for the constant heating rate experiments. For the conversion rates, the corresponding maximum RMS-differences were $7.5 \times 10^{-6} \text{s}^{-1}$ (scaled 13.3%) for the isothermal experiments and $3.0 \times 10^{-5} \text{s}^{-1}$ (scaled 3.4%) for experiments at constant heating rate of 5 K min$^{-1}$. Scaled RMS-differences of $m/m_0$ and $dX/dt$ in the isothermal experiments are generally higher owing to the low overall conversion or mass loss at the low temperatures ($<503 \text{ K}$) for which those experiments were repeated.

Experimental data from thermogravimetric analysis are summarized in Figures 4.1 and 4.2. The data from isothermal experiments clearly reveals differences among the different biomasses in the temperature range 423–523 K. Sunflower husk pellets show the highest mass loss through most of the temperature range tested. The two wood pellets are among the least reactive in the entire temperature range of the isothermal experiments. Pine initially loses mass at rates similar to sunflower, but is less reactive at higher temperatures ($\geq 483 \text{ K}$). The opposite is observed for wheat and beech, for which mass loss accelerates above this temperature. Measured mass loss in oxidative atmosphere differs from that in inert atmosphere from approximately the third isothermal stage (463 K) onward. It was considered whether air entrapped in the sample beds may lead to few, early oxidation reactions, even when the experiments are run with nitrogen atmosphere. However, interstitial air could only supply <0.2% of the oxygen necessary for conversion of the sample, and the entrapped oxygen is additionally expected to diffuse out rapidly. Purge flow rates of 150 mL/min are moreover sufficient to replace the gas volume enclosed in the oven in the first few minutes of the experiment.

For the experiments at constant heating rate, the conversion rate is shown as a function of temperature to allow better comparison with the data available in literature [131–137, 142, 144–146, 158]. With the exception of sunflower, these data does not allow to distinguish between different biomasses and different atmospheres below 473 K. The dominating feature in this data presentation is the peak in conversion rate, typically attributed to reactions of cellulose. Presence of oxygen is seen to accelerate mass loss in all cases, in agreement with published data. However, the effect of oxygen concentration is small, when comparing the experiments under 10% and 20% oxygen atmosphere. The location of the peak decomposition rate is shifted by 5–10 K, and the rates themselves are slightly higher. With oxygen present, two char-
Figure 4.1.: Experimental data from isothermal experiments reveals differences both between biomasses and between heating in oxidative and inert atmosphere in range 423–523 K. From top to bottom: measured (actual) heating profile, measured mass loss (scaled) in 0% oxygen, 20% oxygen and 80% oxygen atmosphere.
Figure 4.2.: Experimental data from 5 K min\(^{-1}\) experiments does not allow to distinguish between fuel (except sunflower) in range 423–523 K. Differences in conversion rate as a function of temperature are most apparent between 523–623 K. From top to bottom: in 0% oxygen, 10% oxygen and 20% oxygen atmosphere.
characteristic peaks can be seen. The secondary peaks in range ≥673 K can likely be attributed to char oxidation.

Dimensionless Biot (Bi), Pyrolysis (Py) and Damköhler (Da) numbers were evaluated to determine the influence of heat transfer limitations (during transient heating) and mass transfer limitations (for oxidation experiments). Heat transfer has negligible influence on the observed mass loss, when internal heat transfer is faster than external heat transfer ($Bi \ll 1$), and when both are faster than reaction rates ($Py \gg 1$) [159, 160]. Mass transfer limitations are considered for oxygen only, and kinetic control can be assumed when diffusion rates are faster than reaction rates ($Da \ll 1$). Additionally, the dimensionless Frank-Kamenetskii-parameter [48] was calculated to determine whether thermal runaway (heat release exceeds internal heat dissipation) could occur in the samples with oxygen present. Details of these calculations can be found in the supporting information. Based on the evaluation of the dimensionless parameters, conditions for the stepwise isothermal experiments were free from heat- and mass transfer limitations. Transport limitations may play a minor role for the experiments at constant heating rate: The Biot number becomes independent of particle or sample size for near-stagnant flows [160]. $Bi$ evaluated to 0.1-0.2 for single particles and $Bi < 0.4$ for the full sample (i.e., the bed of particles). The Pyrolysis number criterion can be used to estimate a critical maximum particle size [160]. Using this approach, kinetic control is predicted up to 700 K (pyrolysis) and 625 K (oxidation) based on modelled rates for the largest particles used (250 µm). Oxygen diffusion limitations were estimated to be wholly negligible below 570 K. By conservative estimate, self-ignition of the samples cannot occur below 530 K under the experimental conditions used, and no self-heating was observed in the experiments. Other possible influences, such as particle specific surface area, particle porosity and bed structure were not quantified. The former two would influence availability of active sites to oxygen attack, while the latter determine diffusion through the sample as well as the bed thermal conductivity. While kinetic control was assumed in interpreting the experiments, the results are strictly valid only for the size range and morphology of the particles used.

4.3. Modelling

Reactions are described by a differential equation for the conversion $X$,

$$\frac{dX}{dt} = k(T) \cdot f_1(X) \cdot f_2(p_{O_2})$$

(4.4)
Kinetic parameters for biomass at self-ignition conditions

$k$ is the rate constant modelled by an Arrhenius-expression,

$$ k = k_0 \cdot \exp \left( -\frac{E_a}{R \cdot T} \right) $$

(4.5)

and $f_1$ and $f_2$ are functions of conversion and oxygen partial pressure, respectively. Most common models for $f_1$ are first- or $n$-order reactions:

$$ f_1(X) = (1 - X)^{n_1} $$

(4.6)

Oxygen-dependent reactions can be modelled by introducing a reaction order in oxygen partial pressure,

$$ f_2(p_{O_2}) = \left( \frac{p_{O_2}}{p_{\text{ref}}} \right)^{n_2} $$

(4.7)

where a reference pressure $p_{\text{ref}}$ is introduced to non-dimensionalize the oxygen partial pressure.

Initial attempts at fitting a single first order reaction to the pyrolysis experiment and combining it with a first order reaction for oxidation yielded poor fits. The quality of the model fit could be improved slightly when an $n$-order reaction was considered. However, fitting only selected temperature ranges of the experimental mass loss curve yielded different sets of kinetic parameters, indicating that a process consisting of several steps was taking place.

Several researchers have linked these steps in the reaction to parallel and independent reactions of the components hemicellulose, cellulose and lignin [133–138, 145, 161]. In this work, extractives are considered as a separate fourth component. Pyrolysis and oxidation of these four components are modelled as parallel reactions, similar to literature [132, 134, 143, 145, 146]. For consistency, char is included as an additional fifth component. Char is defined as the remainder of a complete biomass devolatilization in this model. Char oxidation dominates at higher temperatures, when the volatilizable fractions of hemicellulose, cellulose, lignin and extractives have been removed. Although this process is physically in sequence to pyrolysis and primary oxidation, several authors have demonstrated that, mathematically, it may also be modelled as an additional parallel reaction [133–137]. Following this approach, it is not necessary to track the formation of char. Instead, the biomass components are split into volatilizable and non-volatilizable fractions, i.e. char is considered present already in the unreacted biomass from a modelling point of view. Considering the non-volatilizable fractions as a lumped species, the following mechanism of nine parallel reactions is applied:
Reactions R4.1–4.4 represent pyrolysis of the volatilizable fractions of extractives (XTR), hemicellulose (HC), lignin (LIG) and cellulose (CELL) components. Reactions R4.5–4.8 are the corresponding oxidation reactions. The final reaction R4.9 describes the oxidation of char, regardless of the component or reaction pathway it originates from. The conversion $X_i$ of each of the five species (volatilizable extractives, hemicellulose, lignin and cellulose, plus char) is then described by:

$$\frac{dX_i}{dt} = k_{\text{pyr},i} \cdot (1 - X_i(t))^{n_{\text{pyr},i}} + k_{\text{ox},i} \cdot (1 - X_i(t))^{n_{\text{ox},i}} \cdot \left(\frac{p_{O_2}}{p_{\text{ref}}}ight)^{n_{O_2,i}}$$

(4.8)

where $n$ is the apparent reaction order and the rate constant $k$ is expressed by an Arrhenius law.

$n_{O_2}$ is the reaction order with respect to partial pressure of oxygen $p_{O_2}$. The reference pressure $p_{\text{ref}}$ is used to non-dimensionallize this quantity. Here, $p_{\text{ref}}$ is simply 1 Pa. For char, i.e. the non-volatilizable organic fraction, $k_{\text{pyr}} = 0$. Since only the reacting fractions of the components are considered (i.e. $m_{i,f} = 0$), the remaining mass fraction of each component $i$ is given by

$$w_i(t) = \frac{m_i(t)}{m_{i,0}} = 1 - X_i(t)$$

(4.9)

If $w_{i,0}$ is the original mass fraction of species $i$, then the total mass fraction
is given by:

\[
 w(t) = \frac{m(t)}{m_0} = \sum_i w_{i,0} \cdot w_i(t) \tag{4.10}
\]

The amount of ash is constant. The model requires five parameters for the original mass fractions \(w_{i,0}\), as well as four reaction kinetic triplets \(\{E_{a, i}, k_0, n_{pyr, i}\}\) for the pyrolysis reactions and five sets \(\{E_{a, i}, k_0, n_{ox, i}, n_{O_2, i}\}\) for the oxidation reactions, i.e. a total of 37 parameters per fuel.

In order to reduce the model complexity, the following assumptions are made:

1. The fractions of extractives, hemicellulose, cellulose and lignin can be estimated from the composition analysis (Table 4.1).
2. The total char yield can be determined from the ultimate analysis. The individual char yield of the components extractives, hemicellulose, cellulose and lignin, i.e. the split into volatilizable and non-volatilizable fractions, can be estimated from the behavior of the pure components.
3. Similar sets of activation energies \(E_{a, pyr, i}\) and \(E_{a, ox, i}\) can be found for each component \(i\), regardless of which biomass they appear in. The activation energies can be estimated from the behavior of the pure components.
4. Similar sets of apparent reaction orders in the solid conversion (\(n_{pyr, i}\) and \(n_{ox, i}\)) can be found for each component \(i\), regardless of which biomass they appear in.

By combining the first two assumptions, the original mass fractions \(w_{i,0}\) can be found. The third assumption fixes all activation energies, so they need not be included in the parameter fitting routine. The different biomass conversion models are then defined by 23 parameters: 8 belonging to the four pyrolysis reactions, i.e. \(\{k_0, n_{pyr, i}\}\) and 15 for the additional oxidation reactions \(\{k_0, n_{ox, i}, n_{O_2, i}\}\). Adding the fourth assumption further reduces the biomass-specific parameters to four parameters \(k_0, n_{pyr, i}\) for pyrolysis and five sets \(\{k_0, n_{ox, i}, n_{O_2, i}\}\) for oxidation. It was further evaluated whether a hybrid model of a component-specific pyrolysis model and a lumped species for oxidation can describe the measured data. Assumptions 1-4 are then kept for the pyrolysis mechanism, but replaced with the following for oxidation:

5. Oxidation reactions for the four components extractives, hemicellulose, cellulose and lignin can be modelled with the same set of four kinetic parameters \(\{E_{a, i}, k_0, n_{ox, i}, n_{O_2, i}\}\), which are then specific to each biomass.
6. The oxidation reactions have the same activation energy for all biomasses considered (leaving 3 free parameters per biomass for oxidation).

The model based on assumptions (5) and (6) is referred to as Model I in the
following, the one without those assumptions as Model II. In model I, activation energies from pure component studies were only used in the pyrolysis reactions. However, even if the oxidation reactions are unified in this way, the different volatilizable species need to be tracked individually, as their pyrolysis reactions are different.

The original mass fractions $w_{i,0}$ for volatilizable extractives, hemicellulose, lignin and cellulose, as well as char can be calculated from the composition shown in Table 4.1. Some estimations are made to account for the balance error in determining the composition, as well as the split between volatilizable and char-forming fraction of each component: Extractives (ethanol-soluble) and lignin (Klason) are taken as measured. Cellulose was determined by subtracting the hemicellulose-glucose from the total glucose. For beech, pine and sunflower, the hemicellulose-glucose was measured by acid hydrolysis. The two wood pellet samples appeared to have a carbohydrate composition somewhere in between beech (hardwood) and pine (softwood). The hemicellulose-glucose was therefore approximated with 0.02 kg kg$^{-1}$ for both samples (beech: 0.037 kg kg$^{-1}$, pine: 0.016 kg kg$^{-1}$ – compare Table 4.1). All measured glucose in wheat was assumed to be cellulose. All other organic substance, i.e. the remaining monosaccharides, the uronic acids and the hemicellulose-glucose, was lumped into the hemicellulose component. The sum of these four components is then normalized to one. Char yields from commercial cellulose, lignin and xylan samples were measured, rounded, and then used to distribute the char among the biomass components, Appendix A.2.3. For modelling, 10% of the char was associated with cellulose, 30% with hemicellulose and 60% with lignin. It was assumed that extractives are completely volatilizable. The model composition of the six biomasses, based on the above, is summarized in Table 4.2.

From isothermal experiments following the same procedure as for the native biomasses, pyrolysis activation energies of 60 kJ mol$^{-1}$ for extractives, 120 kJ mol$^{-1}$ for xylan/hemicellulose, 125 kJ mol$^{-1}$ for lignin and 185 kJ mol$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>Beech wood</th>
<th>Pine wood</th>
<th>Sunflower husks</th>
<th>Wheat straw</th>
<th>Wood pellets I1</th>
<th>Wood pellets I2</th>
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</thead>
<tbody>
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<td>XTR</td>
<td>0.019</td>
<td>0.090</td>
<td>0.085</td>
<td>0.038</td>
<td>0.070</td>
<td>0.070</td>
</tr>
<tr>
<td>HC</td>
<td>0.183</td>
<td>0.207</td>
<td>0.217</td>
<td>0.261</td>
<td>0.204</td>
<td>0.192</td>
</tr>
<tr>
<td>LIG</td>
<td>0.249</td>
<td>0.185</td>
<td>0.197</td>
<td>0.091</td>
<td>0.189</td>
<td>0.205</td>
</tr>
<tr>
<td>CELL</td>
<td>0.320</td>
<td>0.375</td>
<td>0.256</td>
<td>0.384</td>
<td>0.383</td>
<td>0.372</td>
</tr>
<tr>
<td>CHAR</td>
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<td>0.193</td>
<td>0.184</td>
<td>0.149</td>
<td>0.155</td>
</tr>
<tr>
<td>Ash</td>
<td>0.027</td>
<td>0.003</td>
<td>0.052</td>
<td>0.042</td>
<td>0.006</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Table 4.2.: Composition $w_{i,0}$ used in the reaction kinetics model. Data calculated from composition analysis (compare Table 4.1). See text for discussion.
Kinetic parameters for biomass at self-ignition conditions

for cellulose were obtained. Data from these measurements can be found in Appendix A.2.3.

The thermogravimetric data measured in inert atmosphere was then used to determine kinetic parameters of the four pyrolysis reactions. This was carried out in two steps. In the first step, fitting was done by simulating a large series of conversion curves for the isothermal experiments and finding kinetic parameter sets so that the root-mean-square deviations of relative mass remaining and mass loss rate are minimized. The RMS-deviation is defined as

\[ \delta_\phi = \sqrt{\frac{\sum (\phi_{\text{exp}}(t) - \phi_{\text{sim}}(t))^2}{N}}; \quad \phi = \{m/m_0, dm/dt\} \]  

Due to numerical compensation effects, several combinations of \( k_{0,\text{pyr},i} \) and \( n_{\text{pyr},i} \) can model the data from isothermal experiments within a similar error range. Therefore, those parameter sets which best fit the isothermal data were then checked against the data from the 5 K min\(^{-1} \) experiments. The twenty combinations minimizing mass loss error (\( \delta_{m/m_0} \)) and those minimizing error on the mass loss rate (\( \delta_{dm/dt} \)) were compared to the constant heating rate data in this second step. That parameter set from the reduced number of combinations which minimizes the deviation in predicting the conversion rate (i.e., \( \phi = dX/dt \) in the above equation) within 373–773 K was then selected for each biomass. The procedure was repeated iteratively to determine uniform \( n_{\text{pyr},i} \) for the components, regardless of which biomass they appear in (modelling assumption 4).

The same procedure was then applied to the isothermal experiments carried out in oxidative atmosphere. The pyrolysis reactions were modelled by the kinetic parameters obtained previously. For the simpler oxidation model (model I), the fitting procedure was run iteratively to determine a common activation energy for all biomasses. The remaining kinetic parameters (\( k_0, n_{\text{ox}} \) and \( n_{O_2} \)) for each biomass were then found by again simulating curves with a large number of parameter combinations, and selecting those with minimal error. For the more complex scheme (model II), activation energies for oxidation of the volatilizable fractions were determined as 75 kJ mol\(^{-1} \) for extractives, 150 kJ mol\(^{-1} \) for xylan/hemicellulose, 120 kJ mol\(^{-1} \) for lignin and 225 kJ mol\(^{-1} \) for cellulose. These estimates are based on the behavior of the commercial samples when subjected to the same heating program (Appendix A.2.3). In both model I and II (i.e. single- and component oxidation model), the models for 20% and 80% oxygen were optimized simultaneously in order to determine the reaction order in oxygen. Again, the parameter sets that best fit the isothermal data are compared to the non-isothermal experiments, and that set which best represents the conversion rate between
CHAPTER 4

373–773 K was chosen. Char oxidation was assumed to be negligible in the temperature range below 523 K. A simple kinetic calculation was carried out to check this assumption. Char in this case refers to that fraction of the material which cannot undergo further devolutilization. We assume this to be identical with the char as determined in the ultimate analysis. Branca and Di Blasi [136, 138] suggest a single oxidation reaction with $E_a = 185 \text{ kJ mol}^{-1}$ for a completely devolatilized biomass residue. This value was also used here. Pre-exponential factor and reaction order in the solid conversion were then adapted to the experimental data to match the char peaks apparent in Figure 4.2. The shift in char peaks from the experiments at 10% and 20% oxygen apparent in the data can be represented with a reaction order between 0 and 1. Here, the reaction order in oxygen for char was fixed at 0.5, which falls within the lower end of the range of values reported in the literature [134, 145, 162]. It should be emphasized that optimizing the kinetics for char oxidation is not in focus of this work.

4.4. Results and Discussion

The kinetic parameters fitted to the six biomasses are found in Tables 4.3, 4.4 and 4.5 for the pyrolysis model, oxidation model I and oxidation model II, respectively.

Table 4.3.: Kinetic data for the pyrolysis models. Differences between biomasses are modelled by different pre-exponential factors $k_{0,pyr}$. Apparent activation energies and reaction orders of the components are uniform for all biomasses, with the exception of cellulose $n_{pyr}$: Beech: 0.9, Pine: 1.1, Sunflower: 1.7, Wheat: 2.0, Wood pellets I1: 1.1, Wood pellets I2: 1.1

<table>
<thead>
<tr>
<th>Component</th>
<th>Extractives</th>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{a,pyr}$ [kJ mol$^{-1}$]</td>
<td>60</td>
<td>150</td>
<td>125</td>
<td>185</td>
</tr>
<tr>
<td>$n_{pyr}$ [-]</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
<td>(0.9–2.0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biomass</th>
<th>$k_{0,pyr}$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech</td>
<td>$1.6 \times 10^3$</td>
</tr>
<tr>
<td>Pine</td>
<td>$8.0 \times 10^2$</td>
</tr>
<tr>
<td>Sunflower</td>
<td>$1.2 \times 10^3$</td>
</tr>
<tr>
<td>Wheat</td>
<td>$1.0 \times 10^3$</td>
</tr>
<tr>
<td>Wood pellets I1</td>
<td>$4.0 \times 10^2$</td>
</tr>
<tr>
<td>Wood pellets I2</td>
<td>$6.0 \times 10^2$</td>
</tr>
</tbody>
</table>
Table 4.4.: Oxidation model I: kinetics for oxidation of a lumped volatilizable component and char. The same char kinetics are used in oxidation model II.

<table>
<thead>
<tr>
<th>Extr./Hemicell./Lig./Cell</th>
<th>Char</th>
<th>$E_a$ [kJ mol$^{-1}$]</th>
<th>$k_0$ [s$^{-1}$]</th>
<th>$n_{ox}$ [-]</th>
<th>$n_{O2}$</th>
<th>$k_0$ [s$^{-1}$]</th>
<th>$n_{ox}$ [-]</th>
<th>$n_{O2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech</td>
<td></td>
<td>130</td>
<td>2.00 x 10$^7$</td>
<td>2.2</td>
<td>0.45</td>
<td>5.7 x 10$^9$</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Pine</td>
<td></td>
<td></td>
<td>1.04 x 10$^7$</td>
<td>1.25</td>
<td>0.40</td>
<td>5.0 x 10$^8$</td>
<td>0.55</td>
<td>0.5</td>
</tr>
<tr>
<td>Sunflower</td>
<td></td>
<td></td>
<td>1.62 x 10$^7$</td>
<td>2.5</td>
<td>0.50</td>
<td>5.0 x 10$^8$</td>
<td>0.65</td>
<td>0.5</td>
</tr>
<tr>
<td>Wheat</td>
<td></td>
<td></td>
<td>1.49 x 10$^7$</td>
<td>1.6</td>
<td>0.50</td>
<td>5.7 x 10$^9$</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Wood pellets I1</td>
<td></td>
<td></td>
<td>7.52 x 10$^6$</td>
<td>2.2</td>
<td>0.45</td>
<td>1.1 x 10$^9$</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Wood pellets I2</td>
<td></td>
<td></td>
<td>5.60 x 10$^6$</td>
<td>2.5</td>
<td>0.45</td>
<td>4.2 x 10$^8$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 4.5.: Oxidation model II: kinetic data for the component-dependent oxidation model. No contribution of extractives was seen, i.e. $k_{0,ox} = 0$ for this component. Char kinetic data for this model are the same as in Table 4.4. All activation energies, as well as the reaction orders of the components hemicellulose and lignin are uniform for all biomasses.

<table>
<thead>
<tr>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{a,ox}$ [kJ mol$^{-1}$]</td>
<td>200</td>
<td>120</td>
</tr>
<tr>
<td>$n_{ox}$ [-]</td>
<td>1.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$k_{0,ox}$ [s$^{-1}$]</th>
<th>$n_{ox}$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech</td>
<td>2.45 x 10$^{15}$</td>
<td>2.2</td>
</tr>
<tr>
<td>Pine</td>
<td>5.0 x 10$^{14}$</td>
<td>0.6</td>
</tr>
<tr>
<td>Sunflower</td>
<td>6.5 x 10$^{14}$</td>
<td>3.7</td>
</tr>
<tr>
<td>Wheat</td>
<td>1.0 x 10$^{15}$</td>
<td>1.8</td>
</tr>
<tr>
<td>Wood pellets I1</td>
<td>4.0 x 10$^{14}$</td>
<td>0.9</td>
</tr>
<tr>
<td>Wood pellets I2</td>
<td>8.5 x 10$^{14}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$n_{O2}$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech</td>
<td>0.4</td>
</tr>
<tr>
<td>Pine</td>
<td>0.4</td>
</tr>
<tr>
<td>Sunflower</td>
<td>0.5</td>
</tr>
<tr>
<td>Wheat</td>
<td>0.5</td>
</tr>
<tr>
<td>Wood pellets I1</td>
<td>0.5</td>
</tr>
<tr>
<td>Wood pellets I2</td>
<td>0.3</td>
</tr>
</tbody>
</table>
The same pyrolysis-and char oxidation kinetics are used with oxidation models I and II. Modelled mass losses compared well to the isothermal experiments for pyrolysis and both oxidation models. Figure 4.3 shows the comparison for model I. Results for oxidation model II are very similar and can be found in Appendix A.2.4. Differences between the two oxidation models were more apparent when compared to the experiments with a constant 5 K min\(^{-1}\) heating rate (Figure 4.4). Results from this work show that some (but not all) parameters of the kinetic models can be obtained from pure component studies. The models are evaluated for numerical, rather than physical or chemical accuracy - i.e., the model representations of extractives, hemicellulose, lignin and cellulose cannot fully capture the complex behavior of these components as they are found in the biomasses. Additionally, structural influences and component interactions are necessarily convoluted in the kinetic parameters in the proposed scheme of independent and parallel reactions.

Results from modelling pyrolysis and oxidation kinetics are discussed separately below.

### 4.4.1. Pyrolysis kinetics

The kinetic parameters found could explain the experimental data both for the isothermal experiments and those at 5 K min\(^{-1}\). Table 4.6 lists the scaled root-mean-square deviations between model and experiment. Scaled deviations between model and measurement are similar in magnitude to the scaled deviations among repeated experiments (compare section 4.2.2). The values found for the activation energies are moreover in good agreement with those

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(\delta_S(m/m_0))</th>
<th>(\delta_S(dX/dt))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>isothermal [%]</td>
<td>ramp [%]</td>
</tr>
<tr>
<td>Beech</td>
<td>0.84</td>
<td>3.60</td>
</tr>
<tr>
<td>Pine</td>
<td>4.44</td>
<td>6.51</td>
</tr>
<tr>
<td>Sunflower</td>
<td>1.83</td>
<td>5.13</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>2.40</td>
<td>4.39</td>
</tr>
<tr>
<td>Wood pellets I1</td>
<td>5.13</td>
<td>4.95</td>
</tr>
<tr>
<td>Wood pellets I2</td>
<td>4.75</td>
<td>5.68</td>
</tr>
</tbody>
</table>

Table 4.6: Scaled root-mean-square deviations (\(\delta_S\)) between modelled and measured data in inert atmosphere. "Isothermal" refers to the stepwise isothermal experiments, "ramp" to those at constant heating rate 5 K min\(^{-1}\).
Figure 4.3.: Oxidation model I: comparison of isothermal experiments and models for six biomasses, assuming that the oxidation of hemicellulose, cellulose, lignin and extractives can be modelled by the same set of kinetic data. Kinetic parameters are listed in Tables 4.3 and 4.4.
Figure 4.4.: Oxidation model I and II: comparison of experiments at constant heating rate and models for six biomasses, assuming uniform (model I) and separate oxidation kinetics (model II) of hemicellulose, cellulose, lignin and extractives. Symbols represent experimental data, lines are modelled data. Kinetic parameters are listed in Tables 4.3, 4.4 and 4.5.
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found in the literature (e.g., as reviewed in [100, 101]).

An initial loss of mass (423–443 K) could be associated with high amounts of extractives in pine and sunflower (both 9%), although this effect was absent in both wood pellet samples (each 7% extractives), compare Figures 4.1, 4.3 and Table 4.1. The model predicts that extractives are pyrolyzed to a large degree (70–90%) in the isothermal experiments. However, extractives make up only a small part of the biomasses. In the full temperature range of the isothermal experiments, 423–523 K, pyrolysis of the six biomasses is dominated primarily by the decomposition of hemicellulose (25–65% conversion) and, secondly, of lignin (15–25%). An exception is sunflower husk pellets, where the model predicts a slightly lower mass loss of lignin compared to cellulose (6% and 10%, respectively). Modelled mass losses of the cellulose component are otherwise low in this temperature range (1–11%). Additionally, pure cellulose did not show any significant pyrolytic conversion below 503 K (see Appendix A.2.3). In the experiments at 5 K min$^{-1}$ heating rate, a near-complete devolatilization of all biomass samples is observed. This is also captured in the model, as conversion rates approach zero at 773 K in Figure 4.4.

The activation energy found in the xylan experiments, 125 kJ mol$^{-1}$, does not represent the hemicellulose components of all biomasses in the 5 K min$^{-1}$ constant-heating-rate experiments very well. A value of 150 kJ mol$^{-1}$ provides a better agreement between model and measurement. The increased value can be justified by the inhomogeneous nature of hemicellulose (compare Table 4.1), which varies among plant species [85, 87, 88]. Thermal behavior of hemicelluloses may differ substantially, depending on their composition [88, 90–92]. Xylan is thermally less stable than most other hemicelluloses [91]. A higher activation energy for the heterogeneous hemicelluloses of the six biomasses is therefore plausible.

Owing to its low conversion in the isothermal experiments, the free parameters of the cellulose component in the pyrolysis model (i.e., $k_{0,pyr,CELL}$ and $n_{pyr,CELL}$) could not be reliably established from the isothermal experiments. Kinetic parameters were therefore adapted to match the peak seen in the conversion rate/temperature plots (Figures 4.1 and 4.4). Inorganic elements present in the biomass are known to catalyze pyrolysis of the cellulose component [86, 155]. For several biomasses, it has been shown that the temperature of peak conversion rate is decreased with increasing potassium content [155, 163, 164]. The data for the biomasses investigated here agree with these reported trends, and this can be used to calculate the pre-exponential factors $k_{0,pyr,CELL}$ of cellulose pyrolysis from the potassium content. For an activation energy of 185 kJ mol$^{-1}$, the pre-exponential factors can be linearly
correlated with the potassium mass fraction \( w_K \) by

\[
    k_0,\text{pyr,CELL} = (9.34 \times 10^{15} \cdot w_K + 2.37 \times 10^{12} \pm 2.29 \times 10^{12}) \cdot s^{-1} \tag{4.12}
\]

to reproduce the temperatures of peak decomposition rate. Details can be found in Appendix A.2.5. The apparent reaction order in the solid was then set to match the value of the peak decomposition rate. Catalytic effects of inorganic elements have also been used to model hemicellulose pyrolysis [165]. In our experiments, catalytic effects seemed to be smaller than compositional effects for hemicellulose pyrolysis. The inorganic content could therefore only be used to predict cellulose kinetic parameters, but not those of the other components.

The different biomasses can be compared in an Arrhenius plot, Figure 4.5. The sum of the modelled rate constants \( k_i \) is plotted over \( 1/T \), i.e.

\[
    k_{\text{tot}}(T) = \sum_i k_{0,i} \cdot \exp\left(-\frac{E_{a,i}}{R \cdot T}\right); \quad i = \{ \text{XTR, HC, LIG, CELL} \} \tag{4.13}
\]

In the above expression, \( k_{\text{tot}} \) does not take the degree of conversion into account, since this depends on the time-temperature history of the samples. The slope of a curve on an Arrhenius plot is proportional to \(-E_{a}/R\), i.e., the thermal behavior of the biomasses can be compared in this way. The plot shows a high-temperature and a low-temperature regime for all six biomasses, with a transition region at ca. 450–550 K. At temperatures below the transition region, the slope of the curves approach that of the extractive component (60 kJ mol\(^{-1}\)). For temperatures above the transition region, the slope of the curve roughly corresponds to that given by the hemicellulose component (150 kJ mol\(^{-1}\)), and would asymptotically approach that of the cellulose component if extrapolated further (above \( \approx 1000 \) K). In practical experiments, the hemicellulose is depleted already at lower temperatures, so the measured rates become dominated by cellulose kinetics around 600 K (see e.g. [98, 100, 138, 166]). By comparison with Figure 4.2, the transition region (450–550 K) is not well resolved in experiments with constant heating rate of 5 K min\(^{-1}\) or above, which make up the majority of TG-data reported in the literature. This may explain why models fitted to such data do not explain kinetics at these temperatures (and below) very well. The plot also illustrates the relative reactivity of the six biomasses. Sunflower has the highest reaction rate over the entire temperature range, while the reactivity of wheat increases most over the range evaluated. This compares well to experimental data (Figures 4.1 and 4.2). Pine appears more reactive at low temperatures and less reactive at high temperatures. This can be explained by its high amount of extractives (low temperature behavior, <500 K) on one
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Figure 4.5.: Arrhenius plot of the pyrolysis models. Solid lines represent the interval 423–523 K of the stepwise isothermal experiments. The dashed lines extend to 373 K and 773 K, respectively, covering the range of the constant heating rate experiments. The inset magnifies the region 465–540 K.

hand, and by the low reactivity of its hemicellulose and cellulose components (see $k_{0,\text{pyr}}$ in Table 4.3) on the other (high temperature behavior, $>550$ K). In comparison, wheat has a high content of cellulose and a low content of lignin, resulting in a steeper gradient (high activation energy of cellulose component) at the high temperature end of the graph than those seen for other biomasses. The model behavior in the transition zone is explained by both the composition and the reactivity of the individual components. The analysis also shows that no single property of the biomass determines its pyrolysis behavior over the entire temperature range. Rather, rates appear to change from being extractives-dominated, to a hemicellulose-controlled range, and finally to a combined cellulose-hemicellulose controlled regime.
4.4.2. Oxidation kinetics

Both oxidation models I and II are in agreement with data from the stepwise isothermal experiments at 20% and 80% oxygen concentration. In model I, an apparent activation energy of 130 kJ mol$^{-1}$ describes the oxidation of the volatile fractions of extractives, hemicellulose, lignin and cellulose in the temperature range of 423–523 K. The corresponding reaction orders in oxygen are between 0.4 and 0.5 (model I, Table 4.4). Similar rates are found in this region as the sum of hemicellulose, lignin and cellulose kinetics (model II, Table 4.5). Both oxidation models give a quality of fit similar to the pyrolysis models, where the quality of fit is measured by the scaled root-mean-square deviations between model and experiment (Appendix A.2.4). From the standpoint of numerical accuracy, there is no reason to prefer one model over the other in describing the TGA-experiments. The reason why model II, despite its larger number of parameters, does not give a significantly better fit may be due to the constraints placed on some of these parameters – most notably, setting the activation energies to constant values derived from pure component measurements.

The most apparent difference between models I and II is how the overlap between hemicellulose and cellulose oxidation is described at temperatures within 520–670 K, Figure 4.4. Model I predicts a flatter conversion rate profile, with lower peak rates (pine, wood pellets) and a more smooth drop in conversion rates. The higher maximum conversion rates of pine and both wood pellets ($0.0014$ s$^{-1}$, $0.0012$ s$^{-1}$) can be modelled by initially low cellulose oxidation rates, that rapidly accelerate at higher temperatures (>550 K). However, the lower reactivity of cellulose at temperatures below ≈550 K is compensated by a higher hemicellulose reactivity to model the mass loss observed in the stepwise isothermal experiment (model II). This leads to an over-estimation of conversion rates between 520–570 K (Figure 4.4, especially pronounced for both wood pellet samples and pine). The onset behavior (≈450–520 K) of sunflower in the 5 K min$^{-1}$ experiments is only approximated by the pyrolysis model and both oxidation models. This could possibly be traced to the parameters of the hemicellulose model.

Differences in modelling the individual components also appear in the stepwise isothermal experiments, although nearly the same total mass loss is predicted by both models for each biomass. The general trend is that model I predicts higher conversion of the cellulose component and a lower hemicellulose conversion up to 523 K, compared to model II. In model I, conversion of hemicellulose is within 45–70% for the six biomasses, lignin within 30–55% and cellulose 25–55%. In comparison, model II predicts 55–90% conversion for hemicellulose, 20–65% for lignin and 5–25% for cellulose. In general,
the conversion of the components is qualitatively proportional to the total conversion for the six biomasses, i.e., biomasses with a high degree of conversion of hemicellulose also have high degrees of conversion of lignin and cellulose. More details can be seen in Appendix A.2.6. Predicted conversion of extractives does not differ much between the two oxidation models and is in the range of 70–90% for the six biomasses. The values given refer to conversion as the combined effect of pyrolysis and oxidation.

The apparent activation energy for oxidation found in model I (130 kJ mol\(^{-1}\)) falls in the middle of the range of values reported in the literature [77, 111, 130]: 90–210 kJ mol\(^{-1}\). It should be noted that these literature values were derived without separating oxidation and pyrolysis reactions. Activation energies found for model II are also comparable to those reported in the literature: 70–294 kJ mol\(^{-1}\) for hemicellulose, 54–289 kJ mol\(^{-1}\) for lignin and 70–295 kJ mol\(^{-1}\) for cellulose [133, 134, 137, 143-145, 161]. A direct comparison is difficult owing to the different reaction models chosen by different authors. As for the pyrolysis model, the apparent activation energy for hemicellulose (200 kJ mol\(^{-1}\)) was set higher than that of the xylan experiments (150 kJ mol\(^{-1}\)). Apparent reaction orders in oxygen of the cellulose component are slightly > 1, which is somewhat unexpected, and probably a result of the numeric fitting routine. For model II, no contribution of extractives oxidation was found. This will be discussed further below.

The oxidation models can be compared using the same type of Arrhenius plot as for the pyrolysis experiments, as shown in Figure 4.6. Both models are evaluated as combined rates of oxidation and pyrolysis reactions. Similar to the pyrolysis model, a transition region around 450–550 K can be seen. In the low temperature range of the plot (< 450 K), the overall apparent rate is mainly dependent on the pyrolysis of extractives \(E_a \approx 60 \text{ kJ mol}^{-1}\). The contribution of the oxidation reaction is more pronounced from 500 K and upwards (compare Figure 4.5), which is also where predictions of the two oxidation models begin to diverge. Model II generally predicts higher rates \(k_{tot}\), while the order of biomasses with respect to reactivity is similar in both models over a broad temperature range (with sunflower, wheat and beech the most, and wood pellets I2 and pine the least reactive above 525 K). In comparison with measured data (Figures 4.1 and 4.2), conversion rates of beech and wheat exceed those of sunflower at higher temperature (> 503 K in Figure 4.1). This is also reflected in the pre-exponential factors in both oxidation models (Tables 4.4 and 4.5), but not seen in the Arrhenius plot for model I, and visible only for temperatures above 550 K in model II. For model II, the rates \(k_{tot}\) are strongly influenced by the pre-exponential factor for oxidation of cellulose (Table 4.5) above 525 K, so that beech is modelled most reactive at higher temperatures (> 625 K). For model I, the pyrol-
Figure 4.6.: Arrhenius plot of the oxidation models for model I (top) and II (bottom), evaluated at $p_{O_2} = 20$ kPa. Solid lines represent the interval 423–523 K of the stepwise isothermal experiments. The dashed lines extend to 373 K and 773 K, respectively, covering the range of the constant heating rate experiments. The insets magnify the region 465–540 K.
Kinetic parameters for biomass at self-ignition conditions

ysis kinetics of cellulose determine the order of biomasses on the Arrhenius plot. The contribution of the global oxidation reaction to the modelled rate is weak, owing to its lower activation energy \( E_{\text{ox}} = 130 \text{ kJ mol}^{-1} \), compared to \( E_{\text{pyr,CELL}} = 185 \text{ kJ mol}^{-1} \) and \( E_{\text{pyr,HC}} = 150 \text{ kJ mol}^{-1} \).

Conversion-free rates \( k_{\text{tot}} \) can also be calculated from published reaction mechanisms for pine [133, 134, 137]. The model presented in [134] gives \( k_{\text{tot}} \)-rates very similar to model I. The model presented in [133] for pine is also in fair agreement with our model II from temperatures of 500 K and above, and gives rates \( k_{\text{tot}} \) that are slightly higher below this temperature. Evaluating a third model [137] gave significantly higher rates than the ones found here.

The absence of extractives oxidation in model II was unexpected, as spontaneous oxidation of extractives can occur at very low temperatures (303–323 K) [82, 108] and with low activation energies (as low as 55–60 kJ mol\(^{-1}\)) [81, 82]. Reactions at very low temperatures (<400 K) and with low activation energies are difficult to detect in the experimental program used, however. As briefly discussed above, the rate \( k_{\text{tot}} \) becomes increasingly dominated by higher activation energy reactions (especially of hemicellulose) with higher temperatures, and reactions with \( E_a < 60 \text{ kJ mol}^{-1} \) are drowned out. At the low temperature stage of the isothermal experiments (423 K), the lowest measurable reaction rates were in order of \( 10^{-6} \text{ s}^{-1} \), and this is also represented in the model (compare Figures 4.5 and 4.6). At this point, mass loss due to pyrolysis and oxidation could not be distinguished (Figure 4.3). Oxidation of extractives would therefore require significantly higher rates than those of their pyrolysis to be visible in the experiments. Moreover, extractives could also have been partially evaporated rather than pyrolyzed or oxidized in the experiments. Boiling points of C8:0–C18:0 fatty acids are in a range of 510–630 K, with corresponding enthalpies of evaporation 50–122 kJ mol\(^{-1}\).

Similar to the pyrolysis kinetics, no clear correlation between composition (Table 4.1) and reactivity (Figure 4.6) was found. One trend that can be seen is that biomasses rich in potassium (sunflower, wheat; and to a lesser extent, beech) are more reactive at temperatures above ≈500 K than those with low amounts of alkali and alkaline earth metals (pine, both wood pellet samples). This tendency agrees with the trend observed for pyrolysis. Qualitatively, the same observation as for pyrolysis can be made: total reaction rates are dominated by (pyrolysis) extractive kinetics at low temperatures (<450 K) and become increasingly controlled by hemicellulose and cellulose at higher temperatures (model II) or the combination of oxidation of the lumped volatilizable species and pyrolysis of hemicellulose and cellu-
lose (model I). The role of lignin is difficult to distinguish, and its reactions appear to take place in the background. Consequentially, the kinetic parameters determined for the lignin component in model II (Table 4.5) are very similar to the global parameters determined in model I (Table 4.4) for the lumped volatilizable component.

4.5. Conclusions

Owing to its high reactivity at low temperatures, biomass may self-heat and spontaneously ignite when kept or processed in hot environments (>423 K) such as power plant mills. Thermogravimetric analysis of stepwise isothermal experiments at 423–523 K was carried out for six biomasses: two wood species (beech, pine), two commercial wood pellet samples, and two agricultural residues (wheat straw and pelletized sunflower husks). These data were modelled by a reaction scheme considering oxidation and pyrolysis separately, and by modelling biomass as the sum of volatilizable hemicellulose, cellulose, lignin and extractives, as well as a non-volatilizable, combustible fraction (char), and ash as inert component. The pyrolysismodel (Table 4.3) of four volatilizable components was in good agreement with measured data in nitrogen atmosphere. The mechanisms also compared favorably to further experiments carried out between 373–773 K at a constant heating rate of 5 K min$^{-1}$.

For the oxidation process, two different approaches were considered. In the first model (model I, Table 4.4), the volatilizable components were treated as a lumped species, i.e. modelled by the same oxidation kinetic parameters. In an alternative model (model II, Table 4.5), the oxidation of volatilizable hemicellulose, cellulose, lignin and extractives were treated separately. Both models compared well with experimental data for stepwise isothermal experiments at 423–523 K in 20% and 80% oxygen atmosphere. Oxidation (globally, i.e. for the lumped volatilizable component) had an apparent reaction order in oxygen of 0.4–0.5. The oxidation models could with fair accuracy also be applied to experiments at 373–773 K with a constant heating rate of 5 K min$^{-1}$ under 10% and 20% oxygen atmosphere. Differences between the two oxidation models were mainly found in the predicted degree of conversion of hemicellulose and cellulose. For the global mass loss in the temperature range of 423–523 K, the simpler oxidation model is considered as sufficiently accurate, and considering oxidation of the components separately does not offer an advantage.

Some simplifications to the oxidation and pyrolysis models were possible. It was found that activation energies for the biomass components could be set
Kinetic parameters for biomass at self-ignition conditions
to the same value, regardless of which biomass they appear in. In this work, activation energies were fixed to values derived from experiments on commercial cellulose, lignin and xylan samples. This is to be understood as a numerically, rather than physically correct description of the mass loss kinetics. Values found for activation energies were consistent with those published in the literature. The models developed here mainly differ from previous work in the description of the low temperature range (423–523 K). This could especially be seen in a change from a low-temperature regime <450 K, which appeared dominated by extractive kinetics, to a higher temperature regime >500 K, which is controlled mainly by reactions of hemicellulose and, to a lesser extent, by cellulose (Figures 4.5 and 4.6). Biomass rich in extractives (sunflower, pine) correspondingly appeared most reactive at the lower end of the investigated temperature range, whereas biomass with large potassium content (possibly catalyzing cellulose conversion) showed larger mass loss rates (wheat, sunflower) at the upper end of the temperature range.

The kinetic models presented here can be used in simulations of low temperature conversion processes, especially self-heating, self-ignition and smoldering combustion of pulverized biomass. While some trends could be observed, there does not appear to be a strong coupling between any single component and the observed reactivity of the different biomasses. Further research combining composition information and kinetic parameters may be able to shed more light on the relation between the two.

Acknowledgements

The authors thank Ørsted A/S and Energinet for financial support of this work. Tareq Abdulrahman is thanked for assisting in the TGA measurements. Marvin Masche is acknowledged for providing the wood pellet samples and additional analysis data.

4.6. Symbols and abbreviations

<table>
<thead>
<tr>
<th>symbol</th>
<th>quantity</th>
<th>base units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>Biot number</td>
<td>–</td>
</tr>
<tr>
<td>$E_a$</td>
<td>apparent activation energy</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$k_0$</td>
<td>pre-exponential factor</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$m$</td>
<td>mass</td>
<td>kg</td>
</tr>
<tr>
<td>$N$</td>
<td>number of data points</td>
<td>–</td>
</tr>
<tr>
<td>$n$</td>
<td>apparent reaction order</td>
<td>–</td>
</tr>
</tbody>
</table>
**CHAPTER 4**

\[
\begin{align*}
p & \quad \text{pressure} \quad \text{Pa} \\
R & \quad \text{universal gas constant} \quad \text{J mol}^{-1} \text{K}^{-1} \\
T & \quad \text{temperature} \quad \text{K} \\
t & \quad \text{time} \quad \text{s} \\
w & \quad \text{mass fraction} \quad \text{kg kg}^{-1} \\
X & \quad \text{conversion} \\
\delta_\varphi & \quad \text{deviation of } \varphi \\
\delta_{S_\varphi} & \quad \text{scaled deviation of } \varphi
\end{align*}
\]

**indices**

0 \quad \text{initial}

exp \quad \text{experiment}

f \quad \text{final}

ox \quad \text{oxidation}

pyr \quad \text{pyrolysis}

ref \quad \text{reference}

sim \quad \text{simulation}

vol \quad \text{volatilizable}

CELL \quad \text{cellulose}

HC \quad \text{hemicellulose}

LIG \quad \text{lignin}

XTR \quad \text{extractives}

**abbreviations**

RMS \quad \text{root-mean-square}

TGA \quad \text{thermo-gravimetric analysis}
5. Measuring self-heating and thermal runaway of biomass

5.1. Introduction

Solid organic materials may self-heat, smolder and spontaneously ignite, when oxygen is sufficiently available and heat dissipation to the surroundings poor. Smoldering is generally undesirable and has been studied mainly in the context of hazard prevention, as it may be a precursor to fires of stockpiles and in storages and process equipment, of insulation material used in buildings, or wild fires. Smoldering has recently also been suggested as a method of producing biochars [167] and for waste treatment [168]. Self-ignition has therefore been widely studied experimentally, covering a broad range of materials. A large fraction of such studies, e.g. [61–63, 65, 66, 70] has been dedicated primarily to determining conditions critical for ignition, i.e. the size of a material accumulation, its residence time, and the ambient temperature it is stored at. Critical ambient temperatures leading to ignition and sample sizes are frequently correlated based on the thermal ignition theory of Frank-Kamenetskii [48]. While this provides correlations that are numerically simple, few general conclusions can be drawn from such data.

Several researchers have investigated the effects of ambient oxygen [59, 66, 69, 70], water [69, 70, 72] and particle size [67, 72], as well as chemical composition on critical ignition conditions: lower ambient oxygen concentrations generally allow storage at higher ambient temperatures. Water as humidity or moisture can have both promoting and inhibiting effects on self-ignition of biomass [64]. For coals, samples of smaller particles ignite at lower temperatures than those made of coarse particles [67, 72]. Finer pine bark samples were also more reactive than coarser particles [167]. High lignin content in biomasses was found to increase reactivity [73], as was a high volatile content in coals [61, 72]. Further research has aimed at finding other indices (besides self-ignition temperatures) to rank different materials [63, 69, 73, 76, 77]. Mainly, these are values derived from thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC). Conclusions drawn from these single parameters alone are however also of limited use, and they are not as widely documented for different materials and/or differ-
CHAPTER 5

Different operating conditions to allow for meaningful comparative studies.

The motivation of this work is to understand the origin and onset of fires in power plant mills that are used to grind wood pellets and other biomass fuels. This includes the effect of ambient conditions as well as the effects of material properties on self-heating and thermal runaway. Kinetic models for several biomasses have been determined previously (Chapter 4). This part of the study is concerned with how reaction kinetic properties relate to heat and mass transfer in smoldering and igniting dust accumulations. Controlled heating experiments and measurement of product gas emissions can be used to study these phenomena [69, 76, 167]. The experiments also provide a dataset that is used in validating a model for self-heating and ignition in fixed beds (see the following Chapter 6).

5.2. Experimental methods

5.2.1. Setup and procedure

Self-heating and self-ignition were investigated on lab-scale using a horizontal tube oven, Fig. 5.1. All sample materials were either fine grains or powders. Samples were filled lightly (without compaction) into a cylindrical wire mesh basket (length 150 mm, diameter 30 mm), which was placed centrally in a tubular oven (length 955 mm, inner diameter 51 mm). Heat was supplied externally in three segments, which are independently controlled by three thermocontrollers. Further documentation is found in Appendix A.3.1.

Mixtures of nitrogen and oxygen were supplied at one end of the oven, and the gas was extracted at the opposite end, creating a constant flow through the oven. The oven was otherwise closed towards the surroundings and operated at slight overpressure (20-100 mbar) to prevent air leakage into

![Figure 5.1.: Experimental setup for self-heating experiments, simplified](image-url)

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the system. The extracted gases were filtered, dried and analyzed continuously. Gas concentrations that were recorded are CO (range: 0–4000 ppm and 0–30%), CO$_2$ (0–3000 ppm and 0–20%) and O$_2$ (0–25%). Two detectors each were used for CO and CO$_2$ to detect both minor amounts (at reaction onset) and larger amounts during rapid reactions (after ignition/during burnout). Biomass samples also released considerable amounts of condensable tars during the experiments. These accumulated at the (cooled) outlet of the oven as well as in the filters and gas sampling lines. Some tars were removed via the gas conditioning condenser, but they generally could not be collected in a defined way in this setup (and were therefore not analyzed).

Temperatures were measured with 1.5 mm-diameter type-K thermocouples supported by the sample holder. One thermocouple was positioned on the axis of the cylinder, one on the upper boundary and a third in the immediate vicinity of the samples. An additional thermocouple (not shown in Figure 5.1) measured the oven wall temperature at some distance from the sample. All values were recorded in 10 second intervals. Further details on instrumentation and data sampling are found in Appendix A.3.2, more on the procedure in Appendix A.3.3.

Temperature- and gas measurements experience different signal delays. Temperature measurements are nearly instantaneous and only limited by the thermal lag (i.e. heat capacity) of the thermocouple. This effect was neglected. The gas species measurements are delayed due to flow through the conditioning system and considerable length of tubing between oven and analyzer. This was corrected by time-shifting the gas analyzer signal based on the signal response to a pulse of oxygen. The time shift was determined for each experiment individually, and was typically in the order of 2 minutes. Details can be found in Appendix A.3.4.

5.2.2. Materials

Four biomasses were used in this study: beech wood, pine wood, commercial sunflower husk pellets and wheat straw. Beech and pine were selected as typical representatives of hard- and softwood. Sunflower husks and wheat straw represent two typical agricultural residues used as fuels, where sunflower husks are comparatively rich in extractives. Extractives are thought to promote self-ignition [108, 110]. All materials were used in pulverized form. Relevant data are summarized in Table 5.1. Glucose is mainly found in cellulose, with the remaining carbohydrates forming hemicelluloses. The composition in terms of biopolymers is described in more detail in Chapter 4. Additional experiments were carried out with commercially acquired cellu-
Table 5.1.: Proximate, elemental and compositional analysis of the biomasses used in this study. Difference to one in the sum of the compositional analysis is balance error.

<table>
<thead>
<tr>
<th></th>
<th>Beech wood</th>
<th>Pine wood</th>
<th>Sunflower husks</th>
<th>Wheat straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size [µm]</td>
<td>0-200</td>
<td>50-200</td>
<td>125-850</td>
<td>200-400</td>
</tr>
<tr>
<td>Heating value (daf) [MJ kg(^{-1})]</td>
<td>19.15</td>
<td>19.80</td>
<td>20.46</td>
<td>18.20</td>
</tr>
<tr>
<td>Proximate analysis, dry base [kg kg(^{-1})]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatiles</td>
<td>0.771</td>
<td>0.856</td>
<td>0.756</td>
<td>0.774</td>
</tr>
<tr>
<td>Char</td>
<td>0.202</td>
<td>0.141</td>
<td>0.193</td>
<td>0.184</td>
</tr>
<tr>
<td>Ash</td>
<td>0.027</td>
<td>0.003</td>
<td>0.052</td>
<td>0.042</td>
</tr>
<tr>
<td>Moisture (average, from TGA)</td>
<td>0.059</td>
<td>0.049</td>
<td>0.085</td>
<td>0.061</td>
</tr>
<tr>
<td>Elemental analysis, dry base [kg kg(^{-1})]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.512</td>
<td>0.528</td>
<td>0.521</td>
<td>0.480</td>
</tr>
<tr>
<td>H</td>
<td>0.057</td>
<td>0.061</td>
<td>0.059</td>
<td>0.057</td>
</tr>
<tr>
<td>O</td>
<td>0.429</td>
<td>0.410</td>
<td>0.503</td>
<td>0.457</td>
</tr>
<tr>
<td>N</td>
<td>0.002</td>
<td>0.001</td>
<td>0.015</td>
<td>0.004</td>
</tr>
<tr>
<td>Compositional analysis, dry base [kg kg(^{-1})]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-glucose carbohydrates</td>
<td>0.225</td>
<td>0.228</td>
<td>0.273</td>
<td>0.333</td>
</tr>
<tr>
<td>Glucose (total)</td>
<td>0.337</td>
<td>0.440</td>
<td>0.270</td>
<td>0.424</td>
</tr>
<tr>
<td>Klason lignin</td>
<td>0.346</td>
<td>0.278</td>
<td>0.316</td>
<td>0.208</td>
</tr>
<tr>
<td>Extractives</td>
<td>0.015</td>
<td>0.093</td>
<td>0.089</td>
<td>0.039</td>
</tr>
<tr>
<td>Sum (composition)</td>
<td>0.923</td>
<td>1.039</td>
<td>0.948</td>
<td>1.004</td>
</tr>
<tr>
<td>Lignin ash</td>
<td>0.009</td>
<td>0.002</td>
<td>0.006</td>
<td>0.014</td>
</tr>
</tbody>
</table>

lose (Sigma-Aldrich C6288), lignin (alkali; Sigma-Aldrich 471003) and xylan (from cornstalk; abcr Chemie AB143294). Xylan was used as a model compound to represent hemicellulose. Carbon content for these three substances was estimated from data found in the Phyllis2-database [129]. Char content of cellulose, lignin and xylan was estimated based on thermogravimetric analysis (TGA), as the residue from heating to 773 K in inert atmosphere.

5.2.3. Operating conditions

Experimental conditions are given by gas flow rates of oxygen and nitrogen, initial oven temperature (at sample insertion), heating rate, and final oven temperature. A first series was run to determine critical final oven temperatures for self-ignition. Influences of heating rate, oxygen concentration, total gas flow rate, sample bulk density/total mass and particle size were investigated. This series was run for only one material (pine wood). Final oven temperatures were varied in 5 K intervals, using a fresh sample on each run.

In the second set of experiments, the heating rate was fixed to 1 K min\(^{-1}\). Final temperatures oven setpoint temperatures were 573 K (native biomasses)
or 623 K (isolated cellulose, lignin, hemicellulose). With oxygen present, these oven temperatures were sufficient to induce thermal runaway in all cases.

Mill fires are likely linked to dust beds settling and remaining in the mill for prolonged periods of time, rather than to heating by hot transport air (see Chapter 2.2). Gas flow rates in the experiment were typically 2.5 L min\(^{-1}\) (at standard conditions), to mimic settled dust accumulations in near-stagnant atmosphere. Resulting gas velocities around the sample are in order of 0.03 m s\(^{-1}\) at standard conditions. Actual flow velocities will be slightly higher due to higher temperatures and net release of gas from the sample. Comparison of the experimental settings to mill conditions is discussed in Appendix A.3.6.

5.2.4. Evaluation of experiments

The time series data for temperature and gas concentrations give a qualitative understanding of the experiment. In comparing different experiments, heating and reaction progress are more aptly described by the sample center temperature than by time. It is expected that thermal runaway will first occur at a hot spot in the sample center and then spread outwards (compare [48,57]). Reaction progress can be followed by the gas concentrations of CO, CO\(_2\) and O\(_2\), as well as by the temperature distribution within the sample. Heat transfer is monitored by comparing the temperatures at different locations within the sample and in the oven.

Measured volume fractions of CO and CO\(_2\) are influenced both by their rates of production, as well as by the total gas flow rate. To isolate the production from dilution effects, measured volume fractions \(y\) of CO and CO\(_2\) are converted to molar rates by:

\[
\dot{n}_i = y_i \cdot \dot{V}_{g, STP} \cdot \frac{p_{STP}}{RT_{STP}}; \quad i = \text{CO}, \text{CO}_2
\]

(5.1)

In the above, \(\dot{V}_{g, STP}\) the volumetric flow rate at standard temperature and pressure (STP), and the factor \(p_{STP}/(RT_{STP})\) comes from relating volume and molar quantity by the ideal gas law. The gas flow rate \(\dot{V}_{g, STP}\) is estimated from the setpoint values at the oven inlet. Increase in flow rate due to net gas production by reaction is neglected. Since production rates of CO and CO\(_2\) also depend on the available carbon, rates \(\dot{n}\) were scaled by initial sample mass \(m_0\) when different experiments were compared.

Differences between sample and oven temperatures show the direction of net heat transfer: Heat is added to the sample when the difference between sam-
ple and oven is negative \((T_{\text{sample}} - T_{\text{oven}} < 0)\), while the sample gives off heat to the surroundings if the difference is positive. Onset of self-heating cannot be directly detected from this comparison, as self-heating and external heat transfer to the sample may occur simultaneously. The relative contributions of self-heating and external heating are discussed in the following section 5.3.

Values derived from the time-series data are used as indices to characterize the behavior of the samples. These include the point of equal sample center and oven temperatures (“adiabatic” temperature \(T_{\text{ad}}\)); the maximum temperature reached in the sample center \(T_{\text{max}}\); the sample center temperature at which threshold amounts of CO and CO\(_2\) are measured (onset temperatures \(T_{\text{on},i}\)); the integral mass of carbon found in CO and CO\(_2\) \((m_{C,i})\); carbon conversion to CO and CO\(_2\) \((X_C)\); conversion of the total organic fraction \((X_{\text{tot}})\) and integral mass of oxygen consumed \((m_{O_2})\). The index \(i\) is used for chemical species.

Values \(T_{\text{ad}}\) and \(T_{\text{max}}\) are read directly from the time-series data. The temperature \(T_{\text{ad}}\), which is influenced both by heat transfer and heat release, has also been used as a reactivity index in e.g. [69]. It is similar, but not necessarily equal to the crossing-point temperature (equal center and surface temperatures within the sample) proposed by Chen and Chong [57, 58].

Onset values of CO and CO\(_2\) are defined to be as low as possible, and yet well above the calibration offset and noise on the analyzer signal. A value of 10 ppm is sufficiently large for the equipment used here. Scaling by typical values of initial mass and gas flow rates gives \(\dot{n}_{\text{on}}/m_0 := 2 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}\) as appropriate threshold. The corresponding temperature is defined as \(T_{\text{on},i}\).

Integral masses of carbon in CO and CO\(_2\) are calculated from the measured mole fractions \(y\) of CO and CO\(_2\) by:

\[
m_{C,i} = M_C \cdot \int (y_i \cdot \dot{V}_{g,\text{STP}}) \, dt \cdot \frac{P_{\text{STP}}}{RT_{\text{STP}}}; \quad i = \text{CO, CO}_2
\]

where \(M_C\) is the molar mass of carbon. The conversion of fuel carbon to CO and CO\(_2\), \(X_C\) is calculated as:

\[
X_C = \frac{m_{C,\text{CO}} + m_{C,\text{CO}_2}}{m_{C,\text{fuel}}}
\]

The carbon conversion is calculated assuming a moisture content of 5% for all samples, using the initial mass \(m_0\) and the carbon mass fraction listed in Table 5.1. Total conversion \(X_{\text{tot}}\) is calculated from the ratio of reacted organic mass to original mass of the reactive organic substance \(m_{r,0}\). Under oxidizing conditions, the reactive organic is equivalent to the dry and ash-free mass (eq. 5.4). Under pyrolysing conditions, the reactive organic is the
Measuring self-heating and thermal runaway of biomass
dry, ash-and-char-free matter (eq. 5.5):

\[ X_{\text{tot}} = \frac{m_{r,0} - m_{r,f}}{m_{r,0}} = \frac{(1 - w_W) \cdot m_0 - m_f}{(1 - w_W - w_A) \cdot m_0}; \quad y_{O_2} > 0 \] (5.4)

\[ X_{\text{tot}} = \frac{m_{r,0} - m_{r,f}}{m_{r,0}} = \frac{(1 - w_W) \cdot m_0 - m_f}{(1 - w_W - w_A - w_{CH}) \cdot m_0}; \quad y_{O_2} = 0 \] (5.5)

where \( w_A, w_{CH} \) and \( w_W \) are the initial mass fractions of ash, char and moisture, respectively.

Similar to carbon mass in CO and CO\(_2\), the mass of oxygen consumed in the experiment is calculated from measured mole fractions:

\[ m_{O_2} = 2 M_O \cdot \int ((y_{O_2,\text{in}} - y_{O_2,\text{out}}) \cdot V_{g, \text{STP}}) \cdot \frac{p_{\text{STP}}}{R T_{\text{STP}}} \] (5.6)

where \( M_O \) is the molar mass of (atomic) oxygen. The mass-based formulation is used for consistency with the carbon calculations. Specific oxygen consumption is here defined as total mass of oxygen consumed per initial sample mass,

\[ X_O = \frac{m_{O_2}}{m_0} \] (5.7)

### 5.3. Transport limitations

The experimental conditions were checked in simple engineering estimates to determine (1) whether or not diffusion of oxygen may limit reaction rates, and (2) under what conditions heat from the reacting sample would contribute more to the temperature increase in the sample than the heat supplied by the oven. Both were estimated for pine as a reference material. Heat release rates and oxygen consumption rates were estimated assuming: a single oxidation reaction; 20% oxygen in the surroundings; 101 325 Pa ambient pressure. Only the main results of the estimations are summarized below. Further values used and the complete calculations can be found in Appendix A.3.6. In addition to interpreting experimental observations, these estimate calculations are also used to check the plausibility of modelling results (Chapter 6).

#### 5.3.1. Diffusion limitations

Oxidation reactions can become mass-transfer limited at high temperatures: reaction rates increase exponentially, while diffusion rates increase only with
a power of 1.5–2.0 [169] in temperature. The Damköhler-number Da is defined as the ratio of reaction rate (species consumption) to mass transfer rate (diffusion). Kinetically-controlled regimes are characterized by Da < 1, Da > 1 is a diffusion-controlled regime. The Damköhler-number is estimated by

$$Da = \frac{k_{O_2} C_{O_2,stoich} L^2}{D C_{O_2,amb}}$$

(5.8)

where $k_{O_2}$ is the rate at which oxygen is consumed, $C_{O_2,stoich}$ the concentration of oxygen required for complete conversion, $C_{O_2,amb}$ the concentration of oxygen in the surroundings and $D$ the diffusion coefficient. $L$ is a characteristic length, in this case, the sample radius. From an estimated Damköhler-number, oxygen diffusion into the sample is much faster than oxygen depletion in reactions up to around 550 K, Fig. 5.2. The transition region between kinetic and diffusion control is within approximately 500–600 K. In this formulation, the reaction rates are estimated by their upper bound, as depletion of both solid and oxygen (which lowers reaction rates) is neglected (see Appendix A.3.6 for calculation and further discussion). A full, time and space resolved comparison of oxygen consumption and diffusion is found in

Figure 5.2.: The estimated Damköhler-number for oxygen consumption/diffusion in fixed bed experiments shows that the reaction is kinetically controlled up to at least 500 K. Da is evaluated as a function of temperature for: $k_{O_2} = 5.49 \times 10^8 \text{s}^{-1} \exp(15636 \text{K}/T)$, $D = 6.94 \times 10^{-10} \text{m}^2 \text{s}^{-1} (T/\text{K})^{1.75}$, $C_{O_2,stoich} = 4610 \text{mol m}^{-3}$ (compare eq. 5.8). See Appendix A.3.6 for details.
the following chapter 6.

The Damköhler-number has a second-order dependence on length scale. Increasing the sample size by a factor of three would therefore increase Da by one order of magnitude. In comparison with Fig. 5.2, this would shift the critical temperature for diffusion limitation by ca. 50 K. Typical mill operating temperatures (wood pellets) are around 420 K [12], so that reaction onset even in larger dust accumulations is expected to be kinetically controlled. However, reactions in hot spots far from the surface of a dust bed may experience some diffusion limitations.

5.3.2. Heat transfer

Both self-heating and external heating contribute to temperature increase in the sample, as long as sample temperatures are below oven temperatures. Self-heating has an approximately exponential dependence on sample temperature, while external heating is controlled by temperature gradients between sample (surface) and surroundings. External heat transfer appears as the sum of convective (gas phase-sample) and radiative heat transfer (oven wall-sample). Convective heat transfer increases approximately linearly with the temperature difference between sample and gas phase. Heat transfer by radiation between wall and sample is based on a $T^4$-law, therefore it increases both with temperature and temperature gradient. Ratios of heating rates from reaction $\dot{Q}_R$ to external heating rates $\dot{Q}_{\text{ext}}$ therefore depend both on the temperature of the sample as well as on the temperature difference between sample and ambient (Fig. 5.3). From the estimate calculations, self-heating is expected to have a measurable influence from temperatures of 380–500 K and above. Below this temperature range, self-heating rates are orders of magnitude smaller than external heating rates, as long as even minimal temperature gradients exist.

Both radiation and convection contribute to heat transfer from the oven to the sample. Heat transfer by radiation exceeds that by convection as sample temperatures increase. For the parameters used to create Fig. 5.3, this is the case from $\approx 390$ K upwards. Heat generation from the sample occurs throughout the volume, and therefore also depends on the temperature distribution within the sample. Experiments carried out at different heating rates (1, 5 and $10$ K min$^{-1}$) showed that heating rates of 1 K min$^{-1}$ lead to an approximately uniform temperature distribution in the sample (Appendix A.3.7.1). Homogeneous temperatures in the sample were assumed in the estimate calculations. Capturing the full dynamics of heat transport and heat release requires a time and space resolved model (Chapter 6).
5.4. Results and discussion

5.4.1. Subcritical, supercritical and pyrolyzing conditions

Experiments under subcritical, supercritical and pyrolyzing conditions can be clearly distinguished from their temperature (Fig. 5.4) and gas emission (Fig. 5.5) histories. Pine was used in all four experiments presented. The oven heating rate was 1 K min$^{-1}$ in all cases. Final oven temperatures were 498 K, 503 K or 573 K in these examples. Oxygen volume fractions at the inlet were 20\% or 0\%, total volumetric flow rate of the gas supplied at the inlet was 2.5 L min$^{-1}$. All of the above values are nominal (setpoint) experimental conditions.

Subcritical self-heating is characterized by a mild temperature overshoot (sample temperature exceeds oven temperature by 16 K, Fig. 5.4a), and a very slow decrease in CO and CO$_2$ concentrations (Fig. 5.5a) after reaching a maximum value. Peak temperatures and peak concentrations of CO and CO$_2$ coincide in time. Reactions nearly stabilize and continue for several hours in subcritical experiments. Total conversion $X_{tot}$, conversion of carbon to CO and CO$_2$, $X_C$, and specific oxygen consumption $X_O$ correlate with
Figure 5.4.: Subcritical oxidation, supercritical oxidation and pyrolysis experiments show characteristic time-temperature histories. Conditions in brackets are nominal final oven temperature and nominal oxygen concentration at the inlet. Corresponding gas concentrations shown in Figure 5.5.
Figure 5.5.: CO, CO$_2$ and O$_2$ concentrations of subcritical oxidation, supercritical oxidation and pyrolysis experiments match the temperature profiles shown in Figure 5.4. Conditions in brackets are nominal final oven temperature and nominal oxygen concentration at the inlet.
the duration of the experiment for given temperature and oxygen concentration (see Appendix A.3.7.2). From a dataset of 17 subcritical experiments, $X_{tot}/\Delta t$ correlates with temperature, where $\Delta t$ is the duration of the experiment. Carbon conversion per time $X_C/\Delta t$ and specific oxygen consumption $X_O/\Delta t$ do not show a clear trend with temperature, nor could any relationship between any pair of $X_{tot}$, $X_C$ and $X_O$ be found in subcritical experiments (Appendix A.3.7.2). This implies that CO and CO$_2$ emissions, as well as oxygen consumption are not necessarily proportional to mass loss rates. Species formed in parallel and/or competing pyrolytic reactions are e.g. volatile hydrocarbons and tars (compare e.g. [123, 124]). These observations suggest that oxidation of fuel carbon and formation of pyrolysis products occur at different rates. This is in agreement with thermogravimetric data, where different mass loss characteristics were seen in inert and oxidative atmosphere (Chapter 4). The observation that CO and CO$_2$ emissions are much higher when oxygen is present than in pyrolysis experiments (Fig. 5.5) suggests that these gases mainly allow to follow the progress of oxidation reactions.

Supercritical self-heating results in a sudden (rates up to 60 K min$^{-1}$) and large temperature overshoot ($\approx$300 K, Figs. 5.4b and 5.4c) and significantly higher amounts of CO and CO$_2$ release (Figs. 5.5b and 5.5c). Temperature and gas measurements also match qualitatively during burnout, but peak temperatures are delayed by several minutes compared to peak release rates of CO and CO$_2$. Sample temperatures and off-gas concentrations recede at the end of the experiment. Organic matter is typically consumed completely in supercritical experiments ($X_C > 90\%$ in most experiments). Residues may however contain minor amounts of unreacted char.

Agreement between the measured gas concentrations in the three experiments with oxygen present is generally good up to thermal runaway. Minor differences can be seen up to ca. 100 min. Fig. 5.5 also shows that a volume fraction of 10 ppm can clearly be distinguished from signal fluctuations (noise). Evolution of temperatures and gases at thermal runaway is qualitatively similar (compare Figs. 5.4b/5.4c and 5.5b/5.5c). Some differences are seen in the peak temperatures in the sample center (864.4 K compared to 790.8 K), peak CO volume fraction (5.5% and 5.8%), duration of the burnout phase (216–274 min and 208–274 min), as well as the temperature distribution between sample center, boundary and surrounding gas envelope. These differences can possibly be attributed to a partial collapse of the initially packed bed under ignition, which occurs randomly. This would influence heat transfer, e.g. by exposing formerly insulated hotspots. CO and CO$_2$ emissions seen post-burnout ($t > 270$ min) in Figs. 5.5b and 5.5c likely result from oxidation of residual char.
Behavior of samples heated in inert atmosphere differs markedly from those in oxidative atmosphere, both in temperatures (Fig. 5.4d) and in gas emissions (Fig. 5.5d). Under pyrolyzing conditions, the sample temperature never exceeds that of the oven, and CO and CO$_2$ concentrations are significantly lower during heating. Off-gas concentrations increase with sample temperature and reach a maximum value at the end of the transient heating phase. Pyrolysis reactions recede faster (Fig. 5.5d) and do not show the quasi-stable behavior seen for subcritical self-heating (Fig. 5.5a).

5.4.2. Effect of particle size and sample bulk density

Bulk density was varied by filling different amounts of sample into the same sample holder, i.e. at equal sample volume. Experiments are referred to based on their mass in the following. Two size fractions, fine and coarse were investigated, referring to a sieve fraction of 50–200 µm and 600–1000 µm, respectively. The natural bulk density (i.e., the amount that would fill the sample holder completely, but did not require compaction) of the size fractions varied. For fine pine, it corresponded to 10–12 g, for the coarser sample it was approximately 18 g.

Critical temperatures for thermal runaway are influenced by dust particle size and sample bulk density, Table 5.2. Fine samples 15 g and 18 g, as well as coarse samples 18 g, 19 g and 21 g ignited and burned out, while the other samples showed only subcritical self-heating. Samples of smaller sample mass/bulk density were thus thermally stable at temperatures that lead to ignition of more tightly packed samples. This is expected as a corollary to data reported for solid waste in [69], where ignition temperatures were seen to scale approximately linearly with sample mass.

Carbon conversion and total conversion depended on whether the sample ignited or not, and were otherwise not influenced by sample mass. The amount of oxygen consumed per initial sample mass ($X_O$) was approximately proportional to the degree of carbon conversion $X_C$, which was especially apparent for the supercritical experiments.

For subcritical experiments, the maximum temperature reached scaled linearly with sample mass, from 510 K at 8 g to 528 K at 15 g (coarse sample). In comparison, peak temperatures reached during thermal runaway were scattered with ±40 K around an average value of 810 K, and did not show any trend with initial sample mass. The point of equal sample and oven temperatures $T_{ad}$ was always slightly below the final oven temperature, and varied within ±4 K around a mean of 485 K. The programmed oven heating ramp flattens out at this point (compare Figs. 5.4a and 5.4b for heating programs.
Table 5.2.: Sample mass/bulk density affects onset of thermal runaway and temperatures reached during subcritical self-heating. (Scaled) onset temperatures of CO and CO$_2$ are unaffected by sample mass. All experiments run with pine at 1 K min$^{-1}$ to 498 K nominal oven temperature in 20% oxygen. ‘Fine’ is 50–200 µm size fraction, ‘coarse’ is 600–1000 µm.

<table>
<thead>
<tr>
<th>sample</th>
<th>$m_0$ [g]</th>
<th>$m_f$ [g]</th>
<th>$t_f$ [min]</th>
<th>$X_C$ [%]</th>
<th>$X_{tot}$ [%]</th>
<th>$m_{O_2}$ [g]</th>
<th>$X_O$ [-]</th>
<th>$T_{on,CO}$ [K]</th>
<th>$T_{on,CO_2}$ [K]</th>
<th>$T_{ad}$ [K]</th>
<th>$T_{max}$ [K]</th>
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</thead>
<tbody>
<tr>
<td>fine</td>
<td>8.1</td>
<td>6.1</td>
<td>417</td>
<td>8.7</td>
<td>20.5</td>
<td>1.91</td>
<td>0.24</td>
<td>412</td>
<td>395</td>
<td>484</td>
<td>510</td>
</tr>
<tr>
<td>fine</td>
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<td>20.0</td>
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<td>0.15</td>
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<td>398</td>
<td>487</td>
<td>516</td>
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<tr>
<td>fine</td>
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<td>9.4</td>
<td>347</td>
<td>5.9</td>
<td>17.8</td>
<td>2.45</td>
<td>0.20</td>
<td>417</td>
<td>389</td>
<td>486</td>
<td>521</td>
</tr>
<tr>
<td>fine</td>
<td>15.0</td>
<td>0.68</td>
<td>285</td>
<td>73.8</td>
<td>95.6</td>
<td>14.6</td>
<td>0.97</td>
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<td>390</td>
<td>485</td>
<td>434</td>
</tr>
<tr>
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<td>388</td>
<td>484</td>
<td>820</td>
</tr>
<tr>
<td>coarse</td>
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<td>10.9</td>
<td>414</td>
<td>8.1</td>
<td>23.5</td>
<td>3.01</td>
<td>0.20</td>
<td>423</td>
<td>392</td>
<td>487</td>
<td>528</td>
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<tr>
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<td>350</td>
<td>95.4</td>
<td>95.6</td>
<td>23.0</td>
<td>1.28</td>
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<td>381</td>
<td>486</td>
<td>803</td>
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<td>381</td>
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<tr>
<td>coarse</td>
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<td>1.02</td>
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<td>389</td>
<td>485</td>
<td>813</td>
</tr>
<tr>
<td>mean</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>80.8*</td>
<td>95.0*</td>
<td>-</td>
<td>-</td>
<td>417</td>
<td>389</td>
<td>485</td>
<td>810*</td>
</tr>
</tbody>
</table>

*: supercritical experiments only
Temperature difference between sample and oven depended on sample mass during the initial heating phase, but not once temperatures exceeded $T_{ad}$, Fig. 5.6. Data for coarse 19 g-sample between 330–380 K are likely influenced by a malfunction of the oven controller, and shown for completeness only (see Appendix A.3.7.3). Generally, absolute temperature differences between sample center and oven are larger for larger sample masses between ca. 300–400 K. Differences between the experiments gradually disappear between 450–485 K. The first range is characteristic of external heating, as larger sample masses absorb more heat and therefore are slower to approach the oven temperature. In the second temperature range, self-heating is much faster than external heating. Temperature differences between sample and oven are not dependent on sample mass under those conditions. The temperature range at which self-heating appears is in agreement with the estimated values (section 5.3).

Combined rates of CO and CO$_2$ production $\dot{n}_{CO} + \dot{n}_{CO_2}$ increased exponentially with temperature, and scaled linearly with (initial) sample mass (Fig. 5.7). Corresponding plots of the individual rates $\dot{n}_{CO}$ and $\dot{n}_{CO_2}$ are found in Appendix A.3.7. Both gases show a qualitatively similar behavior (compare also Fig. 5.5). Scaled by initial sample mass, the sum of both rates falls

![Graph showing temperature difference between sample and oven vs. sample temperature]

Figure 5.6.: Sample mass affects the initial heating phase, but not self-heating and ignition. All experiments run with pine at 1 K min$^{-1}$ to 498 K nominal oven temperature in 20% oxygen. ‘Fine’ is 50–200 µm size fraction, ‘coarse’ is 600–1000 µm. Behavior of 19 g-sample due to oven controller fault, see Appendix A.3.7.3.
Figure 5.7.: CO and CO\textsubscript{2} release rates scale with sample mass. All experiments run with pine at 1 K min\textsuperscript{-1} to 498 K nominal oven temperature in 20\% oxygen. ‘Fine’ is 50–200 \textmu m size fraction, ‘coarse’ is 600–1000 \textmu m.

within a narrow band for temperatures in range 370–510 K, Fig. 5.7. The offset of all curves is ±7.5 K on the temperature axis in this interval. Most measurement data collapse onto the same curve, and the scatter is caused mainly by three experiments: the two medium mass coarse pine samples (18 g and 19 g), and the lightest fine dust sample (8 g). These samples nevertheless appear to follow the same exponential increase of $\frac{\dot{n}_{CO} + \dot{n}_{CO_2}}{m_0}$ with temperature, as indicated by the approximately equal slope on the semi-log plot. Onset temperatures of CO and CO\textsubscript{2}, as defined above by a threshold of $\dot{n}_{on}/m_0 = 2 \times 10^{-6} \text{ mol s}^{-1}\text{kg}^{-1}$ were repeatable within ±5 K and ±8 K, respectively (Table 5.2). Igniting samples show a sudden sharp increase of CO and CO\textsubscript{2} production rates with temperature, followed by a phase in which rates become nearly constant with temperature. The former could indicate that additional reactions become relevant on ignition, while the latter suggest diffusion control above $\approx$520–550 K. The temperature range for onset of diffusion control would agree with the estimation made in section 5.3.

For the igniting samples, temperatures at which rates of CO and CO\textsubscript{2} suddenly increase (Fig. 5.7), as well as maximum temperatures, carbon conversion and total conversion do not appear to depend on initial sample mass (Table 5.2), and conversion and maximum temperatures are only weakly correlated. A possible explanation is that the burnout behavior is influenced by the dynamics of the collapsing bed, which is to some degree chaotic and can-
not be predicted from the experimental conditions. Likewise, the different behavior of the coarse and fine 15 g-samples may be due to the difference in specific surface area and/or differences in the bed structure formed by these particles. More systematic investigations of this parameter are necessary to draw further conclusions.

5.4.3. Oxygen availability and mass transfer

Critical temperatures for ignition increased when oxygen was reduced, in agreement with data reported in the literature [59, 66, 69, 70]. Lowering the oxygen concentration from 20% to 8% raises the critical ambient temperature ($T_w$) by approximately 15 K (Table 5.3). In comparison, lowering the oxygen flow rate to the same value as for the 8% case (0.2 L min$^{-1}$ oxygen at the inlet), and adjusting the nitrogen flow rate to attain 20% oxygen (i.e. 1 L min$^{-1}$ total flow rate) does not result in an increased critical temperature. Onset of thermal runaway is therefore limited by oxygen partial pressure, rather than by the total amount of oxygen supplied in these experiments.

Total conversion of the organic fraction and conversion of fuel carbon to CO and CO$_2$ increase with the duration of the experiment (see Appendix A.3.7.2), which varied within this series. The higher conversion rates seen for 8% oxygen are likely due to the higher temperatures at which these experiments were carried out. For experiments with 8% oxygen and 20% oxygen at the same oven temperature, $X_{tot}/\Delta t$ were lower for the lower ambient oxygen concentration (data in Appendix A.3.7.2). Onset temperatures of CO and CO$_2$ release appeared unaffected by oxygen availability, considering that they could fluctuate by ±8 K around a mean value (compare Table 5.2).

Sample burnout may however be limited by oxygen supply (flow rate), in addition to oxygen partial pressure (compare Table 5.3, Figs. 5.8 and 5.9 – additional figures for coarse pine in Appendix A.3.7.4): Temperatures were lower and burnout times were longer for reduced total flow rates at 20% oxygen. Maximum temperatures $T_{max}$ in the sample center for supercritical conditions were highest for 2.5 L min$^{-1}$ and 20% oxygen combinations, slightly lower for 1 L min$^{-1}$ and 20%, and lowest for 2.5 L min$^{-1}$ and 8% oxygen. These trends are seen for both coarse and fine pine samples (Table 5.3). Likewise, mass loss, total conversion of the organic fraction, conversion of fuel carbon to CO and CO$_2$, and consumption of oxygen were highest for experiments at 2.5 L min$^{-1}$ and 20% oxygen under supercritical conditions.

Upon removing the sample from the oven, it was seen that the samples had retained their shape when heated in 8% oxygen, even though temperature and gas emission histories indicated complete burnout (see Appendix
Table 5.3.: Comparison of subcritical and supercritical self-heating for pine. All experiments run with constant heating rate 1 K min$^{-1}$ to final oven temperature, then held at constant temperature. $T_w$ (nom.): nominal final oven temperature, $T_w$ (meas.): measured final oven temperature, $t_f$: duration of experiment, $m_C$: mass of carbon, $X_{C, CO+CO_2}$: conversion of fuel carbon to CO and CO$_2$. (continued on following page)

<table>
<thead>
<tr>
<th>size fraction</th>
<th>50–200 µm</th>
<th>600–1000 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet conditions</td>
<td>2.5 L min$^{-1}$</td>
<td>2.5 L min$^{-1}$</td>
</tr>
<tr>
<td>20% O$_2$</td>
<td>8% O$_2$</td>
<td>20% O$_2$</td>
</tr>
<tr>
<td>$T_w$ (nominal) [K]</td>
<td>498</td>
<td>513</td>
</tr>
<tr>
<td>$T_w$ (measured) [K]</td>
<td>501</td>
<td>517</td>
</tr>
<tr>
<td>$t_f$ [min]</td>
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<td>608</td>
</tr>
<tr>
<td>$m_0$ [g]</td>
<td>10.6</td>
<td>10.8</td>
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<tr>
<td>$m_f$ [g]</td>
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<td>5.75</td>
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<td>$m_C$ [g]</td>
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<td>$m_C$ in CO$_2$ [g]</td>
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<td>0.61</td>
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<tr>
<td>$X_C$ [%]</td>
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<td>16.7</td>
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<tr>
<td>$X_{tot}$ [%]</td>
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<td>44.1</td>
</tr>
<tr>
<td>$m_{O_2}$ [g]</td>
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<td>3.68</td>
</tr>
<tr>
<td>$X_O$ [-]</td>
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</tr>
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<td>$T_{on, CO}$ [K]</td>
<td>408</td>
<td>421</td>
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<td>$T_{on, CO_2}$ [K]</td>
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<td>389</td>
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<tr>
<td>$T_{max}$ [K]</td>
<td>517</td>
<td>536</td>
</tr>
<tr>
<td>Size fraction</td>
<td>Inlet conditions</td>
<td>( T_{w} ) (nominal) [K]</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>50–200µm</td>
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<td>780</td>
</tr>
<tr>
<td>600–1000µm</td>
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</tr>
<tr>
<td>4L min(^{-1})</td>
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<td>416</td>
</tr>
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Table 5.3, continued.
Measuring self-heating and thermal runaway of biomass

Figure 5.8.: Oxygen depletion depends on inlet oxygen concentration and is only slightly influenced by total volumetric flowrate. Data shown for fine pine (50–200 µm), compare Table 5.3. Heating rate 1 K min$^{-1}$ from ambient.

Figure 5.9.: Temperature difference between sample center and oven depends on inlet oxygen concentration and total volumetric flowrate. Data shown for fine pine (50–200 µm), compare Table 5.3. Heating rate 1 K min$^{-1}$ from ambient. Delay in ignition onset for 8% oxygen also due to higher critical ignition temperature.
A.3.7.4): the dust beds shrunk considerably, but remained in their cylindrical shape. Dust beds heated to supercritical ambient temperatures under 2.5 \text{L min}^{-1} and 20\% oxygen collapsed completely, those at 1 \text{L min}^{-1} and 20\% oxygen partially.

5.4.4. Behavior of different biomasses

5.4.4.1. Native biomasses

Samples of beech, pine, sunflower husk pellets and wheat straw differed in their thermal (Fig. 5.10) and gas-release behavior (Fig. 5.11). All experiments were run at constant heating rate 1 \text{K min}^{-1} to a nominal final oven temperature of 573\text{K} in 20\% and 0\% oxygen atmosphere. The raw, time series data can be found in Appendix A.3.7.5. Further data are summarized in Table 5.4, material properties are found in Table 5.1. Bulk density varied between the samples, with the sunflower husk pellets forming much denser beds than the other samples (380 kg m\(^{-3}\) vs. 100-160 kg m\(^{-3}\)). This influences both the critical temperature for thermal runaway (larger heat generation within the same volume), as well as the thermal lag in the external-heating phase (larger heat capacity \(c_p \cdot m\)).

Temperature difference between sample center and oven begin to differ for pyrolysis and oxidation experiments at sample temperatures of 400\text{K} (sun-

![Figure 5.10.: Temperature difference between sample center and oven for different biomasses under oxidizing and pyrolyzing conditions.](image)
Figure 5.11.: Molar production rates of CO and CO$_2$ for different biomasses under oxidizing conditions (top) and pyrolyzing conditions (bottom), scaled by initial sample mass. Experiments were run at 1 K min$^{-1}$ heating rate from ambient to 573 K nominal oven temperature. Compare Table 5.4.
Table 5.4.: Behavior of different biomasses in lab-scale heating experiments. Temperatures are sample temperatures. All experiments run at a constant oven heating rate of 1 K min$^{-1}$ to 573 K final oven temperature (nominal values).

<table>
<thead>
<tr>
<th></th>
<th>Beech wood</th>
<th>Pine wood</th>
<th>Sunflower husks</th>
<th>Wheat straw</th>
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<tr>
<td>at 20% oxygen</td>
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<td>$m_0$ [g]</td>
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<td>12.9</td>
<td>40.0</td>
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<td>$m_f$ [g]</td>
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<td>0.45</td>
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<td>$m_C$ in CO$_2$ [g]</td>
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<td>3.37</td>
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<tr>
<td>$X_{tot}$ [%]</td>
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<td>96.7</td>
<td>103</td>
<td>97.1</td>
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<td>92.7</td>
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<td>81.4</td>
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<td>$X_C(t = t_{ad})$ [%]</td>
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<td>0.55</td>
<td>0.18</td>
<td>0.68</td>
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<tr>
<td>$m_{O_2}$ [g]</td>
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</tr>
<tr>
<td>$X_O$ [-]</td>
<td>1.06</td>
<td>1.28</td>
<td>1.11</td>
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<td>482</td>
<td>442</td>
<td>490</td>
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<td>537</td>
<td>521</td>
<td>522</td>
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<td>813</td>
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<td>428</td>
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<td>373</td>
<td>360</td>
<td>384</td>
</tr>
</tbody>
</table>

|                  |            |           |                 |             |
| at 0% oxygen     |            |           |                 |             |
| $m_0$ [g]        | 17.0       | 10.4      | 40.0            | 11.0        |
| $m_f$ [g]        | 6.97       | 3.36      | 17.7            | 4.36        |
| $m_C$ [g]        | 8.27       | 5.20      | 19.8            | 5.02        |
| $m_C$ in CO [g]  | 0.33       | 0.14      | 0.55            | 0.24        |
| $m_C$ in CO$_2$ [g] | 0.44   | 0.18      | 1.15            | 0.31        |
| $X_{tot}$ [%]    | 74.9       | 77.7      | 71.9            | 76.5        |
| $X_C$ [%]        | 9.32       | 6.13      | 8.60            | 11.0        |
| $T_{on,CO}$ [K]  | 456        | 477       | 424             | 450         |
| $T_{on,CO_2}$ [K] | 395   | 405       | 367             | 391         |
Measuring self-heating and thermal runaway of biomass

flower, pine) and 450 K (beech, wheat), Fig. 5.10. These temperatures are slightly lower than those for which differences in mass loss were detectable in thermogravimetric analysis (≈460 K, compare Chapter 4). Deviations between the pyrolysis and oxidation curves indicate that self-heating contributes to temperature increase in the sample: The slope of temperature difference versus temperature gives a relative measure of exothermicity, with all other parameters assumed equal. Self-heating likely occurs also at temperatures below 400–450 K (as e.g. measured by isothermal calorimetry in [81–83]), but at rates lower than the external heating, compare section 5.3. It is therefore not detectable below that temperature range in these experiments. Pyrolysis of the sunflower husks seems to be mildly exothermic when compared to the other three samples in 0% oxygen atmosphere above ≈470 K. Biomass pyrolysis includes both endothermic and exothermic reactions [100], where the global thermal behavior depends, among others, on sample size and occurrence of secondary char formation [170].

Onset of thermal runaway for beech, pine, sunflower and wheat around 510–540 K can be seen from heating rates exceeding 10 K min⁻¹ (Table 5.4), the ΔT/T-curves approaching a slope of 1 in Fig. 5.10. Additionally, onset of thermal runaway is accompanied by a characteristic jump in the combined CO and CO₂ emission rates (Fig. 5.11) for beech, pine and wheat. Rates of CO and CO₂ approaching a nearly constant value above 520–550 K for all samples again suggests that the burnout regime is diffusion controlled (compare also section 5.3).

Both under oxidizing and under pyrolyzing conditions, relevant amounts of CO and CO₂ are detected from 400 K upwards for all materials. More CO and CO₂ are measured in 20% oxygen atmosphere at all temperatures for all materials. All biomasses show a roughly exponential increase of combined CO and CO₂ production rates with temperature over a broader interval, 400–520 K (as indicated by the straight line on the log-plot). Deviations from the ideal exponential behavior are most apparent for sunflower husks under oxidizing conditions, and for all four materials under pyrolyzing conditions. For pyrolysis experiments, gas release rates cannot be sustained at the end of the experiment (after reaching the final temperature), which can be seen in the vertical drop in Fig. 5.11 (compare also Fig. 5.5d).

Minor differences in onset temperatures of CO and CO₂ among the biomasses were found (Table 5.4). Differences between beech and wheat are likely not significant, as onset temperatures could vary within ±8 K for the same material (pine, compare Table 5.2). Under oxidative atmosphere, sunflower and pine have lower onset temperatures than beech or wheat, which agrees with the kinetic data for these materials (compare Chapter 4). Rates of CO and
CO$_2$ from beech and wheat exceed those from pine at temperatures above 470 K and those from sunflower above 520 K (Fig. 5.11), which is equally in qualitative agreement with thermogravimetric data. Lower emission rates of sunflower at high temperatures >550 K may be due to more severe diffusion limitations. Sunflower samples formed the densest beds, which hinders oxygen access.

In inert atmosphere, CO and CO$_2$ production rates are highest for sunflower within 320–500 K, which also agrees with thermogravimetric measurements. Rates for pine are lowest in the entire temperature range investigated. In comparison, pine showed relatively high (compared to beech and wheat) mass loss rates at low temperatures in thermogravimetric experiments. This further suggests that mass loss and CO and CO$_2$ production are not directly proportional. Likely, extractives responsible for low temperature mass loss form lighter organic compounds instead of CO and CO$_2$ or simply evaporate without thermal decomposition.

Under oxidative atmosphere, all samples show a near-complete conversion of the organic material ($X_{tot}$). Conversion of sunflower exceeds 100 %, which is likely a measurement error (e.g., loss of material while handling the burned out sample). Conversion of carbon to CO and CO$_2$ ($X_C$) is lower than the conversion of all organic material, with the remaining carbon likely forming tars and volatile organic compounds. Only small amounts of carbon are converted to CO and CO$_2$ until $T_{ad}$ is reached. Molar ratios of CO to CO$_2$ under oxidizing conditions vary between 0.13–0.57 (based on total production), 0.22–0.33 (production up to $T_{ad}$) and 0.32–0.73 (based on maximum rates). Threshold values of $y_{CO}/y_{CO_2}$ have been suggested to define ignition [118]. While this ratio appeared to increase suddenly as heating rates increased (Appendix A.3.7.5), values before and after ignition were specific to each biomass. There did not appear to be a single characteristic threshold value valid for all biomasses.

Under inert atmosphere, conversion of the volatilizable organic fraction is considered (see eq. 5.5). Char fractions were estimated based on data found in Table 5.1. Conversion of fuel carbon to CO and CO$_2$ is significantly lower than conversion of the volatilizable fraction. Conversion $X_{tot}$ and $X_C$ in inert atmosphere does not differ much among the biomasses. Ratios of $y_{CO}/y_{CO_2}$ increased markedly with sample temperature in inert atmosphere for all biomasses (Appendix A.3.7.5).
5.4.4.2. Biomass constituents

Behavior of isolated biomass constituents cellulose and lignin resembled that of the native biomasses to some degree, while that of xylan (as a hemicellulose model compound) differed significantly (Figures 5.13 and 5.12, Table 5.5). Heating was continued until final nominal oven temperatures of 623 K. Measured oven temperatures exceeded the setpoint by 5–8 K, and up to 18 K in the xylan-oxidation experiment. All other experimental parameters were the same as in the previous section. The raw, time series data can be found in Appendix A.3.7.5.

Cellulose was characterized by a late onset of measurable self-heating (Fig. 5.12) in oxidative atmosphere, comparatively low production rates of CO and CO$_2$ over most of the temperature range up to 550 K (Fig. 5.13), and high onset temperatures for CO and CO$_2$. On the other hand, conversion of the organic fraction $X_{tot}$ and conversion of fuel carbon to CO and CO$_2$ was in a similar range as that of native biomasses (compare Tables 5.5 and 5.4), both for oxidative and inert atmospheres.

Lignin had lower onset temperatures of CO and CO$_2$ (both in oxidative and inert atmosphere), a lower adiabatic temperature $T_{ad}$ and reached (self-)heating rates of 10 K min$^{-1}$ at a temperature similar to those of the native biomasses (527 K compared to 510-540 K). Lignin additionally reached relatively high temperatures upon ignition, but the burnout phase was short and reactions rapidly declined. Conversion of the total organic fraction $X_{tot}$ as well as conversion of fuel carbon to CO and CO$_2$ ($X_C$) and specific oxygen consumption ($X_O$) were correspondingly low. Under inert conditions, conversion of the total organic fraction was larger than 1 – either because the char content $w_{CH}$ of lignin was overestimated (limiting the ‘available’ mass fraction), or because the burned out sample was not completely recovered (rendering $m_f$ too low). Low conversion of lignin-carbon to CO and CO$_2$ is generally plausible: Smoldering of wood releases significant amounts of phenolic compounds, which likely originate from thermal decomposition of lignin [123].

Xylan was difficult to handle, as it readily absorbed humidity from the ambient and formed sticky agglomerates. Upon removing samples from both pyrolysis and oxidation experiments, it was found that the samples had apparently boiled and spilled over the sample holder (compare also Chapter 3 and Appendix A.1). Residues from both experiments were highly porous, foam-like chars. The char from the oxidation experiment could not be completely retrieved. Formation and collapse of bubbles may also explain the fluctuations in CO and CO$_2$ production rates between 460-510 K (Fig. 5.13). Unlike the other samples, CO and CO$_2$ from pyrolysis and oxidation do not differ much in this temperature range. Only at higher temperatures (>550 K) are...
Figure 5.12.: Temperature difference for cellulose, lignin and xylan

Figure 5.13.: Molar production rates of CO and CO₂ for cellulose, lignin and xylan under oxidizing and pyrolyzing conditions. Experiments were run at 1 K min⁻¹ heating rate from ambient to 623 K nominal oven temperature.
Table 5.5.: Behavior of cellulose, lignin and xylan in lab-scale heating experiments. Temperatures are sample temperatures. All experiments run at a constant oven heating rate of 1 K min$^{-1}$ to 623 K final oven temperature (nominal values).

<table>
<thead>
<tr>
<th></th>
<th>Cellulose</th>
<th>Lignin</th>
<th>Xylan</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_C$ (estimated from [129]) [kg kg$^{-1}$]</td>
<td>0.44</td>
<td>0.63</td>
<td>0.40</td>
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<tr>
<td>$w_{CH}$ (estimated from TGA) [kg kg$^{-1}$]</td>
<td>0.09</td>
<td>0.60</td>
<td>0.25</td>
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<tr>
<td>at 20% oxygen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_0$ [g]</td>
<td>30.0</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>$m_f$ [g]</td>
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<td>25.9</td>
<td>n.a.</td>
</tr>
<tr>
<td>$m_C$ in CO [g]</td>
<td>5.21</td>
<td>0.23</td>
<td>2.44</td>
</tr>
<tr>
<td>$m_C$ in CO$_2$ [g]</td>
<td>4.12</td>
<td>1.59</td>
<td>4.54</td>
</tr>
<tr>
<td>$X_{tot}$ [%]</td>
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<td>33.7</td>
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</tr>
<tr>
<td>$X_C$ [%]</td>
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<td>7.61</td>
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</tr>
<tr>
<td>$X_C(t = t_{ad})$ [%]</td>
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<td>14.3</td>
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<td>3.51</td>
<td>18.4</td>
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<td>454</td>
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<td>107</td>
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<td>$T_{on,CO_2}$ [K]</td>
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<td>466</td>
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</table>
gas production rates higher in oxidative atmosphere than under inert conditions. Xylan possibly follows a two-step process of char formation and subsequent oxidation. Xylan also did not show the typical thermal runaway behavior seen in all other experiments. Peak temperatures reached during burnout were only 20 K higher than the measured ambient oven temperatures. Pyrolysis of xylan is (mildly) exothermal [91], and may have contributed to the heating of the sample (Fig. 5.12).

Early reaction onset of lignin, late onset of cellulose, and little difference between pyrolysis and oxidation of lignin are in qualitative agreement with data from isothermal TGA-experiments (Appendix A.2.3). Ratios of \( \frac{y_{CO}}{y_{CO_2}} \) were in range 0.1–0.2 for lignin (regardless of oxygen availability) and increased mildly with temperature. For both cellulose and xylan, ratios of \( CO \) to \( CO_2 \) increased from approximately 0.2 at 425 K to 0.6 at 600 K, both in oxidizing and inert atmosphere (Appendix A.3.7.5).

With high values of total conversion and conversion of fuel carbon to \( CO \) and \( CO_2 \) after burnout, cellulose most closely resembled the native biomasses. Onset temperatures of \( CO \) and \( CO_2 \), as well as the temperatures showing onset of thermal runaway (\( T_{ad} \) and \( T(dT/dt > 10 \text{ K min}^{-1}) \)) were however significantly higher in cellulose than in beech, pine, sunflower husks or wheat straw.

### 5.4.4.3. Comparison of native biomasses to isolated components

There are several concerns when applying results obtained for isolated components to native biomasses (see Chapter 2.4 for discussion). One point is that components cellulose, lignin and hemicellulose may differ substantially in behavior in isolated form from their behavior in unaltered biomass [88,100]. Another main point is that “hemicellulose” is a generic term for a variety of hexose- and pentose-polymers with different thermal behavior [88,90–92], for which xylan is possibly a poor model compound (despite its widespread use in the literature).

Nevertheless, the earlier reaction onset in lignin oxidation (based on \( CO \) and \( CO_2 \) production rates) may explain why higher reactivity is reported for biomasses rich in lignin [73]. In this study, lignin content varied within 21–35% (Table 5.1), but did not appear to influence any of the critical temperatures used to assess reactivity (compare Table 5.4): beech had the highest, wheat straw the lowest lignin content; yet both materials showed similar behavior in the oven experiments.

Increasing ratios of \( CO \) to \( CO_2 \) used as a reaction onset criterion in [118] may point to a transition from a regime dominated by lignin-decomposition
to one where cellulose reactions become more important, as lignin has low CO/CO₂-ratios over the temperature range investigated (Appendix A.3.7.5). The more or less pronounced jump in combined emission rates with temperature seen for the native biomasses, but not for the isolated components (compare Figs. 5.7, 5.11 and 5.13) suggests a similar interpretation. Superimposing the lignin and cellulose gas emission rates in Fig. 5.13 would give a similar behavior as that seen in Fig 5.11: exponential increase of rates with temperature followed by a sudden sharp increase (and a more moderate increase as oxygen diffusion limits reaction rates). That cellulose is the most thermally stable of the biomass macrocomponents is general consensus. A delayed onset of cellulose decomposition in fixed bed experiments is therefore also plausible.

Conversion of the total organic fraction, and conversion of fuel carbon to CO and CO₂ under oxidative conditions was lower for all of the isolated components than for any native biomass (compare Tables 5.4 and 5.5). This suggests either significant interactions among the macrocomponents in native biomasses and/or significant alteration of the components during the isolation procedure. Chemical interactions between biomass components are discussed in the literature for oxidation [103,108] and pyrolysis [171,172]. The general trend reported is that products from decomposition of one component catalyze reactions of an other. Differences in the physical structure of native biomasses versus isolated components may also influence pyrolysis via e.g. secondary reactions [172]. The particle morphology of the samples was not investigated further in this study, but even from visual inspection it was clear that particles behaved differently. Also, the isolated components formed beds of greater density than the native biomasses (compare sample masses in Tables 5.4 and 5.5).

Ultimately, the connection between behavior of native biomasses and isolated components appears rather loose. Especially the xylan experiments did not fit into the scheme of the other biomasses. Concluding from the isolated components to native biomasses is therefore somewhat tentative. Linking the composition of the native biomasses to their behavior in the fixed bed experiments did not yield any additional information, compared to the reaction kinetic measurements (Chapter 4).

5.5. Conclusions

Lab-scale experiments to measure onset of oxidation reactions and self-heating were carried out by gradually heating (1 K/min) pulverized samples of 10–40 g. Different native biomasses (beech, pine, sunflower, wheat), as well as iso-
lated components (cellulose, lignin and xylan) were investigated. Different ambient oxygen concentrations (0%, 8% and 20% volume fractions) were used to separate pyrolysis from oxidation reactions and to investigate the influence of ambient oxygen. Experiments allowed to clearly distinguish between subcritical (mild self-heating) and supercritical conditions (thermal runaway). Larger bulk densities and higher ambient oxygen concentrations supported thermal runaway. Critical ambient temperatures for ignition were ca. 15K higher when oxygen was reduced from 20% to 8%. The focus of this work was mainly to understand the events leading up to either thermal runaway or stabilization of mild self-heating reactions, while burnout of the samples was of lesser interest.

Reaction onset could be observed by CO and CO$_2$-emissions, which gradually appeared once the samples reached $\approx$350 K. There was always more CO and $\text{CO}_2$ in oxidative atmosphere experiments than in inert atmosphere, which shows that these gases originate mainly form oxidation reactions, with minor contributions from pyrolysis. Emissions scaled with the mass of the sample, and where corrected for this effect for further analysis. Temperatures at which product gases were detected were lower than those for which self-heating contributed to a detectable temperature increase in the sample. Threshold values for the onset of CO and $\text{CO}_2$ (scaled by initial sample mass) were defined as $2 \times 10^{-6}$ mol s$^{-1}$kg$^{-1}$ for each gas. The corresponding temperatures at which these threshold rates were measured (355–465 K for $\text{CO}_2$, 360–525 K for CO – Tables 5.4 and 5.5) were repeatable within $\pm$8 K (as investigated for pine under 20% oxygen). Onset temperatures appeared to be mainly material-specific. In oxidative atmosphere, lignin, sunflower and pine had the lowest onset temperatures. Under inert atmosphere, CO and $\text{CO}_2$ appeared at the lowest temperatures for lignin and sunflower.

Both under oxidative as under inert atmosphere, emission rates increased with temperature in a similar manner for the four native biomasses. In comparison, lignin exhibited a slower increase of CO and $\text{CO}_2$ rates with temperature, cellulose a faster increase than the native biomasses. Xylan appeared to boil when heated, leading to fluctuating release of CO and $\text{CO}_2$, which is difficult to compare to any of the other samples. Lowering oxygen in the ambient from 20% to 8% did not appear to have a significant effect on CO and $\text{CO}_2$ onset temperatures. Removing oxygen access completely however shifted onset temperatures by $+15$–$70$ K (CO) and $+5$–$30$ K ($\text{CO}_2$). Spread between emissions in inert and oxidative atmosphere also depended on the sample material.

Onset of smoldering oxidation reactions, onset of thermal runaway and behavior on burnout were not necessarily correlated: Beech and wheat showed
a later reaction onset (based on CO and CO\textsubscript{2} emission rates) in oxidative atmosphere, but underwent thermal runaway at temperatures lower than pine. Lignin appeared most reactive under low temperatures, but quickly extinguished after ignition, leaving a large fraction of unreacted organic material. Native biomasses showed a sudden increase in CO and CO\textsubscript{2} emission rates with temperature on thermal runaway, which may be linked to a sudden increase in cellulose conversion.

Comparison of different materials generally showed trends similar to thermo-gravimetric data (Chapter 4), suggesting kinetic control in the experiments up to ignition. This is further supported by an estimated Damköhler-number, which indicated that diffusion limitations would first become important above ca. 500–550 K. Based on simple scaling estimations, it is probable that ignition of settled dust beds in power plant mills is equally kinetically controlled. Results from this part of the study are used in the following for model validation (see Chapter 6).

5.6. Symbols and abbreviations

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<th>symbol</th>
<th>quantity</th>
<th>base units</th>
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<td>( C )</td>
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<tr>
<td>( D )</td>
<td>diffusion coefficient</td>
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<td>w</td>
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</table>

**superscripts**

□ □ per unit time (rate of □)

**abbreviations**

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<tr>
<th>daf</th>
<th>dry and ash free</th>
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<tr>
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<td>standard temperature and pressure</td>
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<td>TGA</td>
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6. Modelling self-heating and thermal runaway of biomass

6.1. Introduction

Self-heating and spontaneous ignition can occur in biomass and other organic material. Preventing self-ignition in industrial applications requires additional safety measures, often entailing additional costs. One example is the use of wood pellets and other biomass fuels in combined heat and power plants. Operating temperatures of mills for pulverized fuel boilers need to be lowered to prevent self-ignition on hot surfaces or by hot air streams [12, 34]. This however lowers the overall plant efficiency, as pre-heating of transport air is a method of internally recirculating energy. Therefore, it is desirable to operate at a temperature that is at a minimum distance from critical temperatures for ignition. Self-ignition has been widely studied experimentally. However valuable these studies are in understanding the phenomenon, little has come from them in terms of generalized, predictive models.

Simple models to predict self-ignition have been based on the thermal ignition theories by Semenov [46] and Frank-Kamenetskii [48]. Scaling laws based on these theories relate the sample size in form of a characteristic dimension to critical ambient temperatures for self-ignition. Extrapolating self-ignition temperatures for solid fuels from lab scale to industrial application based on these scaling laws has been shown to lead to unreliable risk assessments [64, 71]. Non-negligible uncertainties when extrapolating from lab scale to application are also acknowledged in the relevant norm EN 15188 [50], which builds on Frank-Kamenetskii’s thermal explosion theory [48].

Some progress has been made with models that go beyond simple correlations of material properties and process parameters. Such studies were either concerned with determining critical conditions for self-ignition, or describing transient smoldering. Smoldering is related to self-heating and spontaneous ignition in that it is a slow, exothermal oxidation process. Sizes of the systems modelled range from small lab-scale experiments [65, 145, 173–175] to pilot-scale setups [174, 176] and large stockpiles [105, 177–179] or silos [120, 173]. Several authors [65, 173, 175] stress the sensitivity of crit-
ical temperatures towards the reaction kinetic model used. However, only few researchers (e.g. [120, 145]) attempt to independently validate their kinetic model.

Several studies [65, 105, 173, 175, 177] use kinetic parameters determined from hot storage tests. Extracting the kinetic parameters from such experiments is based on a Frank-Kamenetskii modelling approach, and the kinetic parameters are not necessarily free from transport limitations. Van Blijderveen et al. [174] model self-heating in a lab-scale packed bed using a zero-dimensional model. They assume ignition is caused by oxidative degradation of hemicellulose, combining heat of reaction of hemicellulose pyrolysis in nitrogen measured in [90] with kinetic rates for hemicellulose degradation in air calculated from [166] (thermogravimetric analysis). The modeling results are in agreement with experiments presented by the same group [180]. Huang and Rein [145] model smoldering of peat, using a kinetic scheme derived from thermogravimetric analysis. The ignition phase however plays only a minor role in their work, which is focused on smoldering once ignition has been achieved. Mahmoudi et al. [176] model ignition in a packed bed. Under their modelling assumptions, ignition occurs by oxidation of volatiles in the gas phase, and direct heterogeneous oxidation of the biomass is neglected.

Works concerning self-ignition of stockpiles of biomass are frequently concerned with the role of biological activity [105, 177, 179]. This was found to be necessary to raise the temperature in model calculations to levels sufficient to initiate pure chemical oxidation. The role of biological activity is however somewhat debated in the literature. Wet stockpiles of bagasse have been observed to self-heat even when treated with biocides [104]. Bacterial and fungal activity is in any case expected to cease above 333–353 K [103–105]. Above this range, chemical oxidation takes over. Absorption of moisture may be an alternative initial source of heat [104, 107, 109]. Condensation induced ignition has been observed experimentally and modelled for lignite [181].

Ignition models based solely on reaction mechanisms of heterogeneous oxidation and parallel pyrolysis are rare in the literature. In this work, the kinetic model previously determined for several biomasses (Chapter 4) is applied to simulations of self-heating and thermal runaway. A further objective is to investigate the influences of various material parameters and transport terms. Lab-scale experiments not used in determining the kinetic model are used for validation. A numerical solver is developed as a tool to meet these objectives. Improvement of simulation codes is specifically not a focus of this work. Rather, it is demonstrated that a simple numerical solver can predict lab-scale experiments in which self-ignition of biomass occurs, provided that
kinetic data are available. A scaling study is included to evaluate whether mill fires can plausibly be explained by self-ignition of settled biomass dusts.

6.2. Modelling

The model is introduced in the following, beginning with the purpose and scope of the model. The system of equations that constitute the model is presented next. Following that, the more technical aspects of the model, e.g. definition of boundary conditions and discretization of the equation system are described. The specific features of the model, such as the reaction mechanism and the material properties are given in the last part of the section.

6.2.1. Model scope

The aim of the model is to predict self-heating and thermal runaway in settled dust beds. The model is formulated for an open system as shown in Figure 6.1. Gas flow in and out of the domain are accounted for ($\dot{m}_{\text{in}}$, $\dot{m}_{\text{out}}$). These streams also carry enthalpy ($H_{\text{in}}$, $H_{\text{out}}$) in and out of the domain. Additionally, heat is exchanged between gas and wall by convection ($\dot{Q}_{g-w}$), between wall and dust bed by radiation ($\dot{Q}_{w-s}$) and between dust bed and contact structure by conduction ($\dot{Q}_{c-s}$). A source term $\dot{Q}_R$ appears in the dust bed due to reaction. The additional terms for mass ($\dot{m}_{s-g}$), enthalpy ($H_{s-g}$), and heat

![Diagram of Modelling Domain](image-url)

Figure 6.1.: Modelling domain, including mass ($\dot{m}$), enthalpy ($\dot{H} = \dot{m} \cdot h$) and heat transfer ($\dot{Q}$) between solid, gas flow and surroundings, simplified.
transfer by convection ($\dot{Q}_{g-s}$) appear between the model zones of dust bed and bulk gas.

The zones surrounding the dust bed (bulk gas, contacting structure, non-contacting walls) are modelled in a simplified way. The rationale for including them is that the boundary conditions are more easily defined for these surroundings than on the surfaces of the dust bed.

The solid consists of several species (components). Each species undergoes an individual set of reactions. The types of reactions in the model are heterogeneous oxidation (R6.1), pyrolysis (R6.2), and evaporation of water (R6.3):

$$\text{organic solid} + \text{O}_2 \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} \quad \text{(R6.1)}$$

$$\text{organic solid} \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} + \text{tars and volatiles} \quad \text{(R6.2)}$$

$$\text{moisture} \rightarrow \text{H}_2\text{O} \quad \text{(R6.3)}$$

Homogeneous gas phase reactions and condensation of water vapor are neglected. The primary motivation for including a species model is determining consumption and availability of oxygen.

### 6.2.2. Governing equations

The model is developed for one dimensional geometries: spheres, infinite cylinders, and infinite slabs. Spatial gradients are resolved along the radius (sphere, cylinder) or the thickness of the dust bed (slab). Actual geometries are simplified so that they can be represented by one of the ideal geometries, Fig. 6.2. The shape of the surrounding wall/enclosure and the bulk flow direction of gases through the domain are not modelled. Surrounding walls can have arbitrary shapes, and concentration gradients in the gas phase perpendicular to the model axis are neglected.

The dust bed contains two phases, the solid (index $s$) and the interstitial gas

![Figure 6.2.: Geometry and boundary conditions.](image-url)
phase (index $g$). Solid in this case refers to the macroscopic structure, e.g. chips, grains or fibers cut from biomass as well as pellets produced from these; as opposed to bulk properties (particle beds, 'superstructure') and cell/fiber walls (microstructure). The split between solid and gas phase is described by the porosity $\phi$,

$$
\phi = 1 - \frac{\rho_{\text{tot}}}{\rho_{s}} = \frac{V_{g}}{V_{\text{tot}}}
$$

(6.1)

where $\rho_{\text{tot}}$ is the bulk density and $\rho_{s}$ the particle density. Additionally, thermal equilibrium between solid and interstitial gas phase is assumed within the dust bed, i.e. $T_{g} = T_{s} = T$. The ideal gas law is used as an equation of state in the gas phase, both for bulk and interstitial gas:

$$
p = C_{g}RT_{g}
$$

(6.2)

Several solid and gaseous species are tracked individually in the model. Density $\rho_{s,i}$ is used in solid species balances and concentration $C_{g,i}$ for individual gaseous species. Total mass balances are calculated from the sum of all species, where $M$ is the molar mass:

$$
\rho_{s} = \sum_{i} \rho_{s,i}
$$

(6.3)

$$
\rho_{g} = \sum_{i} \rho_{g,i} = \sum_{i} M_{i} \cdot C_{g,i}
$$

(6.4)

$$
C_{g} = \sum_{i} C_{g,i}
$$

(6.5)

The dust bed zone is described by the following equations for the mass balance of the solid species (eq. 6.6), the species balance in the interstitial gas phase (eq. 6.7), and the heat balance in the entire dust bed (eq. 6.8):

$$
\frac{\partial \rho_{s,i}}{\partial t} = \dot{n}_{R,s,i}
$$

(6.6)

$$
\frac{\partial C_{g,i}}{\partial t} = -\frac{1}{r \omega} \frac{\partial}{\partial r} \left( r \omega D \frac{\partial C_{g,i}}{\partial r} \right) - \frac{1}{r \omega} \frac{\partial}{\partial r} \left( r \omega u C_{g,i} \right) + \frac{\dot{n}_{R,g,i}}{\phi}
$$

(6.7)

$$
\frac{\partial T}{\partial t} = \frac{1}{\rho_{s} c_{p,s} + \rho_{g} c_{p,g}} \left( -\frac{1}{r \omega} \frac{\partial}{\partial r} \left( r \omega \lambda \frac{\partial T}{\partial r} \right) + Q_{R}^{t} \right)
$$

(6.8)

In the above, $r$ is the spatial coordinate. Gradient terms with $\partial / \partial r$ depend on the geometry, where $\omega = 0$ for slabs, $\omega = 1$ for cylinders and $\omega = 2$ for spheres. The triple dash" on the source terms indicates a volumetric quantity. $D$ is the diffusion coefficient, $u$ the velocity of advective transport, and
\( \lambda \) the effective thermal conductivity of the dust bed. Fick’s law of diffusion and Fourier’s law of heat conduction are applied.

The bulk gas phase is described by species (eq. 6.9) and heat balance (eq. 6.10):

\[
\frac{\partial C_{g,i}}{\partial t} = -\frac{1}{r \omega} \frac{\partial}{\partial r} \left( r^\omega D \frac{\partial C_{g,i}}{\partial r} \right) - \frac{1}{r \omega} \frac{\partial}{\partial r} \left( r^\omega u C_{g,i} \right) + \frac{1}{V_g} \left( \dot{n}_{g,in} - \dot{n}_{g,out} \right)
\] (6.9)

\[
\frac{\partial T}{\partial t} = \frac{1}{\rho_g V_g c_{p,g}} \left( \dot{H}_{g,in} - \dot{H}_{g,out} + \dot{H}_{g,R} + \dot{Q}_\alpha \right)
\] (6.10)

The \( \partial / \partial r \)-terms describe transport along the model axis (diffusion, advection) and are used here to model flow to and from the dust bed. Molar streams \( \dot{n}_{g,in} \) and \( \dot{n}_{g,out} \) and enthalpy streams \( \dot{H}_{g,in} \) and \( \dot{H}_{g,out} \) describe transport over the domain boundary. The term \( \dot{H}_{g,R} \) is the net enthalpy flow from the dust bed to the bulk gas due to gas emissions from the reacting dust bed, and \( \dot{Q}_\alpha \) is the heat transfer by convection between wall and gas as well as between dust bed and gas.

Mass, species and enthalpy balances in the domain are defined by the system of equations 6.3–6.10. In the following sections, expressions for the individual terms appearing in the equations are discussed, geometry and boundary conditions are defined, and the discretization is briefly explained. Further information is also found in Appendices A.4 and A.5.

### 6.2.2.1. Source terms from reactions

In the above equations eq. 6.6–6.8, terms \( \dot{m}_{R,s,i} \), \( \dot{n}_{R,g,i} \) and \( \dot{Q}_R \) are source terms due to reactions. Heterogeneous reactions and decomposition of solids is described by modelling the conversion \( X \),

\[
X_{s,i} = \frac{m_{s,i,0} - m_{s,i}(t)}{m_{s,i,0}}
\] (6.11)

where \( m_{s,i,0} \) is the initial mass of species \( i \). Reactive species are defined to be completely convertible. The model equation for conversion in each reaction \( r \) is

\[
\frac{dX_{s,i,r}}{dt} = k_r \cdot (1 - X_{s,i})^{\nu_{s,i,r}} \cdot \prod_j \left( \frac{p_{g,j}}{p_{ref}} \right)^{\nu_{g,j,r}}
\] (6.12)

A power law dependence on conversion and on the partial pressure of gases \( j \) involved in the reaction is assumed, with \( \nu \) as reaction orders. The reaction
rate constants $k$ are modelled by an Arrhenius equation:

$$k_r = k_0 \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (6.13)$$

As a shorthand notation, a source term density $z_r$ in units [mol m$^{-3}$ s$^{-1}$] for each reaction is introduced, so that

$$z_r = -\frac{\rho_{s,0}}{M_{s,i}} \cdot k_r \cdot (1 - X_{s,i}) \cdot \prod_j \left(\frac{p_{g,j}}{p_{ref}}\right)^{\nu_{g,j,r}} \quad (6.14)$$

In the above equation, $\gamma_{i,r} := -1$ is the stoichiometric coefficient of solid species $i$, i.e. reactions are scaled to consumption of one mole of $i$ per unit volume, and $z_r > 0$. The source terms can then be described by summing over all reactions (with species $j \neq i$):

$$\dot{m}_{R,s,i} = \sum_r \gamma_{s,i,r} \cdot M_{s,i} \cdot z_r \quad (6.15)$$

$$\dot{m}_{R,g,j} = \sum_r \gamma_{g,j,r} \cdot z_r \quad (6.16)$$

$$\dot{Q}_R = \sum_r \Delta H_{R,r} \cdot z_r \quad (6.17)$$

In the above, $\Delta H_{R,r}$ is the heat of reaction in [J mol$^{-1}$]. The stoichiometric coefficients $\gamma_{i,r}$ and $\gamma_{j,r}$ are positive if the species is produced, negative if it is consumed and zero otherwise.

6.2.2.2. Mass transfer in the gas phase

The molecular diffusion coefficient $D$ in eq. 6.7 and 6.9 is influenced by temperature. It can be approximated by:

$$D = D_{ref} \left(\frac{T}{T_{ref}}\right)^{1.75} \quad (6.18)$$

where diffusion coefficients $D_{ref}$ at reference conditions can be found in tabulated form in the literature. The temperature exponent is theoretically limited to the interval of 1.5–2.0 [169], of which the mean is used here. Values suggested in the literature based on measurements are within 1.7–1.81 [182–184]. The pressure gradient that drives the advective transport $u$ in this model appears only due to release of gas and heat from reactions. Within the dust bed, it can be modelled by Darcy’s law as in e.g. [145,175,185–187].
gas velocity $u$ of Darcy flow is given by

$$u = -\frac{\kappa}{\eta} \cdot \frac{dp}{dr}$$  \hspace{1cm} (6.19)

where $\kappa$ is the permeability of the solid in units of [m$^2$] and $\eta$ the dynamic viscosity of the gas in [Pa s]. Since pressure gradients arise only from reactions, they can be expressed as a function of state variables temperature and pressure.

### 6.2.2.3. Heat transfer

The effective thermal conductivity appearing in eq. 6.8 is calculated as a combination of heat conduction in the solid structure and in the interstitial gas phase and by radiation across pores. The equivalent thermal conductivity of gas and solid is calculated from an empirical calculation, superimposing parallel and serial heat conduction [19].

$$\lambda_{\text{eff}} = \lambda_g \cdot \left( \frac{0.2}{K_1} + \frac{0.8}{K_{II}} \right)^{-1}$$  \hspace{1cm} (6.20)

where $K_1$ and $K_{II}$ are the coefficients for serial conduction and parallel conduction, respectively:

$$K_1 = \left( \phi + \frac{1 - \phi}{\lambda_s/\lambda_g} \right)^{-1} \quad \text{and} \quad K_{II} = \phi + (1 - \phi) \cdot \frac{\lambda_s}{\lambda_g}$$  \hspace{1cm} (6.21)

Heat transfer by radiation within the bed (i.e. by radiation across pores) is included with an additive term [188]:

$$\lambda = \lambda_{\text{eff}} + \lambda_\varepsilon \quad ; \quad \lambda_\varepsilon = K_\varepsilon \sigma T^3$$  \hspace{1cm} (6.22)

where $\sigma$ is the Stefan-Boltzmann constant, and the proportionality factor $K_\varepsilon$ depends on pore size and geometry.

### 6.2.2.4. Boundary conditions

At the domain boundaries, the spatial gradients appearing in equations 6.7–6.10 are not continuously defined. Boundary conditions replace the missing values for heat and mass transfer.
**Inflow and outflow**  Gas is transported into and out of the domain via the bulk gas. The inflow of species \( i \) is given by:

\[
\dot{n}_{i,\text{in}} = y_{i,\text{in}} \dot{V}_{\text{in}} \frac{p_{\text{in}}}{RT_{\text{in}}}
\]  \hspace{1cm} (6.23)

where the inlet values of mole fraction \( y \), volumetric flow rate \( \dot{V} \), pressure \( p \) and temperature \( T \) are specified. The molar flow rates at the outlet \( \dot{n}_{i,\text{out}} \) are calculated from the mole fractions in the bulk gas \( y_{i,g} \) and the constant pressure boundary condition:

\[
p(C_g, T_g, \dot{n}_{\text{in}}, \dot{n}_{s-g}) = p_0 = \text{const.}
\]  \hspace{1cm} (6.24)

The pressure in the bulk gas depends on total concentration \( C_g \), temperature \( T_g \), inflow \( \dot{n}_{\text{in}} \) and net exchange of gases between dust bed and bulk gas \( \dot{n}_{s-g} \). Calculation of the molar flow rates \( \dot{n}_{i,\text{out}} \) at the outlet to satisfy the above condition is found in Appendix A.4.2.

The side of the dust bed not in contact with the bulk gas phase is either modelled by a symmetry boundary condition (spheres, cylinders), or as an impermeable wall (slabs). In both cases, the flux of gases is zero across the interface. At the interface between dust bed and bulk gas phase, similar terms appear in eqs. 6.7 and 6.9 to describe diffusion and advection. Gradients \( \partial/\partial r \) can therefore be evaluated continuously on both sides of the interface.

**External heat transfer**  External heat transfer, here expressed as heat flux \( \dot{Q}^* \), appears as radiation between wall and solid (eq. 6.25), convection between gas and solid (eq. 6.26), convection between gas and wall (eq. 6.27), and for slab geometries also as conduction at the solid contact (eq. 6.28):

\[
\dot{Q}_{\varepsilon,\text{w-s}}^* = \varepsilon \cdot \sigma \cdot (T_{\text{w}}^4 - T_{\text{s}}^4)
\]  \hspace{1cm} (6.25)

\[
\dot{Q}_{\alpha,\text{g-s}}^* = \alpha_{\text{g-s}} \cdot (T_g - T_s)
\]  \hspace{1cm} (6.26)

\[
\dot{Q}_{\alpha,\text{g-w}}^* = \alpha_{\text{g-w}} \cdot (T_g - T_w)
\]  \hspace{1cm} (6.27)

\[
\dot{Q}_{\lambda,\text{c-s}}^* = \frac{\lambda_c}{s_c} \cdot (T_c - T_s)
\]  \hspace{1cm} (6.28)

In the above equations, \( \varepsilon \) is the effective emissivity, \( \sigma \) is the Stefan-Boltzmann constant, \( \alpha \) are heat transfer coefficients, \( \lambda_c \) the thermal conductivity of the contacting structure and \( s_c \) its wall thickness. The effective emissivity depends on the emissivities of wall and solid, as well as their geometry (see Appendix A.4.3). The heat transfer coefficients \( \alpha \) are found from Nusselt
number correlations (see Appendix A.4.4). The above are substituted into eq. 6.8 for $\lambda \partial T/\partial r$ and into eq. 6.10 for $\dot{Q}_\alpha = \int \dot{Q}'_\alpha dA$ at the appropriate surfaces.

6.2.2.5. Discretization

The volume of the dust bed is discretized into cells of finite volume along the model axis (Fig. 6.2). Figure 6.3 shows the discretization into cells for long cylinders or spheres. For both cylinders and spheres, the cells have curved surfaces. For slabs, the cells boundaries are planar, parallel surfaces. For cylinders and spheres, symmetry is applied as the inner boundary condition (no heat and mass transfer). For slabs, the inner boundary condition is given by heat conduction through the contact structure. The cell centers are spaced at equal distances. For the curved geometries, this means that the volume of the inner cells is much smaller than the outer cells.

Equations 6.6–6.10 are integrated over finite volume cells (Appendix A.4.1). Changes in the volume $m$ (Fig. 6.3) due to diffusive and advective transport can be expressed by the flux across the boundary to and from neighboring volumes $m-1$ and $m+1$. Boundary conditions (as described above) replace the flux terms at $r_{\text{inner}}$ and $r_{\text{outer}}$.

The balance equations are discretized in time and space and solved iteratively. All quantities are evaluated at the cell midpoints, that are illustrated in Figure 6.3. The point $r = 0$ is a boundary of the inner cell in the one-dimensional model, and not a cell midpoint. The bulk gas is modelled by a single cell.

An implicit scheme (backward Euler) is applied to the diffusive terms (heat conduction, gas diffusion) in equations 6.7, 6.8 and 6.9. Implicit schemes are

![Figure 6.3: Discretization into finite volume cells for long cylinders or spheres. $r$ is the modelling axis. For flat cylinders or slabs, the cell boundaries are planar surfaces.](image)

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unconditionally stable (see e.g. [189]). A first order upwind scheme is used to determine the concentrations in the advective terms \( (C_{g_i} u) \) in equations 6.7 and 6.9. Solutions for the equation system in each timestep are found by an inner iteration loop. The calculation moves on to the next timestep if the inner iteration converges, or a preset number of inner iterations is reached. The width of the timestep is adapted to the heat release and oxygen consumption rates at runtime. This allows the solver to march forward faster when reaction rates are low, while providing better temporal resolution in the ignition phase. More details are found in Appendix A.5.

### 6.2.3. Modelling parameters

#### 6.2.3.1. Reaction mechanism

Kinetic rate parameters and stoichiometry make up the parameters of the reaction mechanism (Table 6.1). Heat release and product gas models are added to the kinetic model developed in Chapter 4. Gaseous species released during smoldering or pyrolysis of biomass are CO, CO\(_2\), water vapor, H\(_2\), hydrocarbons and organic volatiles (e.g., furans and phenolic compounds) [123, 124, 126, 127, 190–192]. With respect to self-heating and ignition, tracking consumption of oxygen is the main purpose of the species

| Table 6.1. | Necessary inputs for the reaction model. Reaction model parameters are specific to each reaction. Stoichiometric coefficients \( \gamma_g \) of gaseous species are calculated from fuel composition and estimated ratios of gaseous species. |
|---|---|---|
| parameter | units | source |
| \( k_0 \) | pre-exponential factor | s\(^{-1}\) | TGA (ch. 4) |
| \( E_a \) | activation energy | kJ mol\(^{-1}\) | TGA (ch. 4) |
| \( \nu \) | reaction order | - | TGA (ch. 4) |
| \( y_{C}, y_{H}, y_{O} \) | organic solid composition | mol mol\(^{-1}\) | elemental analysis |
| \( y_{CO}/y_{CO_2} \) | CO/CO\(_2\)-ratio (oxidation) | - | estimate |
| \( y_{gas}/y_{vol} \) | oxygen distribution (pyrolysis) | - | estimate |
| \( y_{CO}/y_{CO_2} \) | CO/CO\(_2\)-ratio (pyrolysis) | - | estimate |
| \( y_{H_2O}/y_{CO_2} \) | H\(_2\)O/CO\(_2\)-ratio (pyrolysis) | - | estimate |
| \( h_{LHV} \) | lower heating value | kJ kg\(^{-1}\) | fuel analysis |
model. The mechanism consists of the following reactions:

\[
\begin{align*}
\text{XTR} & \xrightarrow{k_1} \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{VOL} \\
\text{HC} & \xrightarrow{k_2} \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{VOL} \\
\text{LIG} & \xrightarrow{k_3} \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{VOL} \\
\text{CELL} & \xrightarrow{k_4} \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{VOL} \\
\text{CHAR} & \xrightarrow{k_9} \text{CO} + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

Reactions labeled \( k_1 \) to \( k_4 \) are pyrolysis reactions, reactions \( k_5 \) to \( k_9 \) are oxidation reactions. XTR, HC, LIG, and CELL are the volatilizable fractions of extractives, hemicellulose, lignin and cellulose, respectively. The non-volatilizable remainder is the species CHAR. Similarly, pyrolysis products that do not form permanent gases \( \text{CO}, \text{CO}_2 \) and \( \text{H}_2\text{O} \) are lumped into a single volatiles species (VOL). Two models were developed for the oxidation reactions, one in which the rate constants \( k_5 - k_8 \) are all equal (\emph{Model I}), and one in which they are independent (\emph{Model II}). Both models were used in this part of the study. The split of the biomass into the five components, as well as kinetic parameters \( k_0, E_a \) and \( \nu \) were derived in Chapter 4, and values used can be found there (Tables 4.2, 4.3, 4.4 and 4.5).

Solving the elemental balances for carbon, hydrogen and oxygen requires to estimate the elemental composition of XTR, HC, LIG, CELL and CHAR, as well as the product gas distribution, i.e. the stoichiometric coefficients \( \gamma_{g,i} \). For simplicity, it is assumed that all five biomass components can be represented by the same organic pseudo-species. Values for \( \gamma_C, \gamma_H \) and \( \gamma_O \) are then specific to each biomass and can be found from an elemental analysis. Composition of the pseudo-species are summarized in Table 6.2. Noting that \( C_5 \) and \( C_6 \)-monomers are the basic building blocks of lignocellulosic biomass, the carbon element fraction is scaled to \( \gamma_C := 30 \text{ mol/mol} \). Ratios between stoichiometric coefficients \( \gamma_{g,i}/\gamma_{g,j} \) were estimated based on fixed bed experiments (compare Chapter 5 and Appendix A.3.7.5), as well as data available in the literature [123, 124, 127, 190, 193, 194]. Values were set specific to each component (but independent of biomass), and are summarized in Table 6.3. The fraction \( \gamma_{\text{gas}}/\gamma_{\text{vol}} \) is the ratio of permanent gases \( \text{CO}, \text{CO}_2, \text{H}_2\text{O} \) to other gases and volatiles., i.e. \( \gamma_{\text{gas}} = \gamma_{\text{CO}} + \gamma_{\text{CO}_2} + \gamma_{\text{H}_2\text{O}} \). Stoichiometric coefficients for the pyrolysis reactions \( k_1 - k_4 \) mainly model the fate of solid oxygen in the biomass.

Heat release rates are assumed proportional to mass loss (compare eq. 6.15...
Table 6.2.: Modelling pseudo-species: properties of the organic fraction and total bulk density. Bulk density varied for pine simulations, depending on the experiment simulated (compare Chapter 5). Typical values were in range of 110–120 kg m\(^{-3}\). Compare also Table 5.1.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Beech wood</th>
<th>Pine wood</th>
<th>Sunflower husks</th>
<th>Wheat straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-species</td>
<td>C(<em>{30})H(</em>{40})O(_{19})</td>
<td>C(<em>{30})H(</em>{42})O(_{18})</td>
<td>C(<em>{30})H(</em>{41})O(_{22})</td>
<td>C(<em>{30})H(</em>{42})O(_{21})</td>
</tr>
<tr>
<td>(\gamma_C/\gamma_H)</td>
<td>0.76</td>
<td>0.72</td>
<td>0.74</td>
<td>0.71</td>
</tr>
<tr>
<td>(\gamma_C/\gamma_O)</td>
<td>1.59</td>
<td>1.71</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>(h_{LHV} [MJ kg(^{-1})])</td>
<td>19.15</td>
<td>19.80</td>
<td>20.46</td>
<td>18.20</td>
</tr>
<tr>
<td>(\rho_s [kg m(^{-3})])</td>
<td>160</td>
<td>76–198</td>
<td>377</td>
<td>104</td>
</tr>
</tbody>
</table>

Table 6.3.: Reaction stoichiometry parameters for oxidation and pyrolysis models. Values adapted from own experimental data (Appendix A.3.7.5) and [123,124,127,190,193,194]

<table>
<thead>
<tr>
<th>Component</th>
<th>oxidation</th>
<th>pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\gamma_{CO}/\gamma_{CO_2})</td>
<td>(\gamma_{gas}/\gamma_{vol})</td>
</tr>
<tr>
<td>Extractives</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Cellulose</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Char</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

and 6.17). The heat of reaction for oxidation reactions is calculated from the lower heating value of the biomass, where incomplete conversion of carbon is neglected:

\[
\Delta H_{R,ox} = h_{LHV} \cdot M_{fuel} - \Delta H_{R,CO,ox} \cdot \frac{\gamma_{CO}}{\gamma_{CO} + \gamma_{CO_2} + \gamma_{H_2O}} \cdot \frac{\gamma_{CO}}{\gamma_{fuel}} \\
\approx h_{LHV} \cdot M_{fuel}
\]

(6.29)

Oxidation of CO to CO\(_2\) has a heat of reaction of \(\Delta H_{R,CO,ox} = 283 \text{kJ mol}^{-1}\) (calculated based on the enthalpy of formation of both gases [195]), while the \(h_{LHV} \cdot M_{fuel}\)-term is \(>10 \text{MJ mol}^{-1}\). The error introduced by neglecting the correction term is approximately 5%. This was judged to be less than the conceptual uncertainty, and the sensitivity to the lower heating value \(h_{LHV}\) was investigated instead of correcting for incomplete oxidation. Pyrolysis is assumed to be thermally neutral (\(\Delta H_{R,pyr} = 0\)). In general, biomass pyrolysis includes both exothermic and endothermic processes [100, 170].

The above assumptions include several simplifications. Elemental composition of cellulose, hemicellulose and lignin differ from each other. Values
can be found e.g. in the Phyllis-2-database [129]: Molar ratios of carbon to hydrogen are between 0.53–0.60 for cellulose and 0.75–1 for lignin; the corresponding carbon to oxygen ratios are 1.17–1.20 (cellulose) and 1.78–3.41 (lignin), while those for whole biomasses fall in between these ratios (compare Table 6.2). Neglecting differences between the components likely overestimates the oxygen content of extractives, as well as the hydrogen and oxygen content of the char component. Furthermore, product gas distribution from biomass components cellulose, hemicellulose and lignin is not constant with time or temperature. Both add uncertainty to the estimates of the stoichiometric oxygen demand. In fixed bed experiments of smoldering and igniting biomass (Chapter 5), it was however observed that oxygen consumption is low until the onset of thermal runaway. Onset of thermal runaway is likely not limited by availability of oxygen, although reaction rates decrease under low oxygen concentrations. It is expected that modelling results are not very sensitive to the estimated stoichiometric oxygen demand.

In reality, decomposition (both thermal and oxidative) of these substances includes several steps, which are here simplified into one pseudo-reaction. Also, interactions among components as such are neglected, and only appear numerically in the rate constant expressions. In natural biomass, components do not exist side-by-side, but are bound in a more complex matrix. Assuming heat release proportional to mass loss is therefore only an approximation.

6.2.3.2. Evaporation mechanism

Water evaporation is treated as a single first-order Arrhenius reaction. Evaporation is treated in a simplified manner, as the self-ignition temperatures in the range of interest in this study (>423 K) are greater than those necessary to dry the samples. An evaporation mechanism is included mainly to replicate the characteristic lag of sample temperature measured around 300–380 K in dynamic heating conditions (compare e.g., Figs. 5.10 and 5.12). Rate parameters used are $k_0 = 3 \times 10^{-7} \text{s}^{-1}$, $E_a = 65 \text{kJ mol}^{-1}$, and the enthalpy of evaporation is $\Delta H_{\text{evap}} = 40.66 \text{kJ mol}^{-1}$. Parameters were found by averaging over literature values [145,146].

6.2.3.3. Material properties

Material properties appear in equations for heat and mass transfer (Table 6.4). Parameters and can be grouped into those of the biomass proper ($\lambda_s$, $\rho_s$, $c_{p,s}$), those of the dust bed ($K_e$, $\kappa$), as well as gas phase properties ($\lambda_g$, $\rho_g$, $c_{p,g}$, $\eta_g$), gas mixture properties ($D_{\text{ref}}$), and radiation parameters ($\varepsilon$). Gas
Table 6.4.: Parameters used in base case simulations. Parameter ranges were taken from the literature, unless otherwise noted. The parameter set for the base case was chosen based on most commonly occurring values.

<table>
<thead>
<tr>
<th>parameter</th>
<th>units</th>
<th>base value</th>
<th>range</th>
<th>source/estimated from</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_s )</td>
<td>Wm(^{-1})K(^{-1})</td>
<td>0.2</td>
<td>0.1-0.6</td>
<td>[16-19]</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>kg m(^{-3})</td>
<td>600</td>
<td>200-1000</td>
<td>[17-19, 193]</td>
</tr>
<tr>
<td>( c_{p,s} )</td>
<td>J kg(^{-1})K(^{-1})</td>
<td>2000</td>
<td>1100-2100</td>
<td>[15, 16, 196, 197]</td>
</tr>
<tr>
<td>( K_e )</td>
<td>m</td>
<td>10(^{-3})</td>
<td>10(^{-5})-10(^{-2})</td>
<td>[145, 185]</td>
</tr>
<tr>
<td>( k )</td>
<td>m(^2)</td>
<td>10(^{-10})</td>
<td>10(^{-12})-10(^{-7})</td>
<td>[178, 185]</td>
</tr>
<tr>
<td>( D_{\text{ref}} )</td>
<td>10(^{-5}) m(^{2}) s(^{-1})</td>
<td>1.5</td>
<td>1.3-2.2</td>
<td>[169, 198]</td>
</tr>
<tr>
<td>( \varepsilon_s )</td>
<td>-</td>
<td>0.8</td>
<td>0.4-0.9</td>
<td>[19, 199]</td>
</tr>
<tr>
<td>( \varepsilon_{w} )</td>
<td>-</td>
<td>0.8</td>
<td>0.6-0.9</td>
<td>[19]</td>
</tr>
</tbody>
</table>

Phase properties are well-established and available in reference works as a function of pressure and temperature. Data is available for various species (e.g., N\(_2\), O\(_2\), CO\(_2\), CO, H\(_2\)O), and therefore not discussed further here. Other parameters are known less accurately or show a higher natural variation. Estimating those parameters and the implications for the model are discussed below. Parameter uncertainties were further evaluated by a sensitivity analysis (see section 6.3 Results).

Material properties of biomass vary widely, depending on plant species and part (e.g., wood or bark), geographic origin and treatment. Solid thermal conductivity \( \lambda_s \), solid density \( \rho_s \) and specific heat capacity \( c_{p,s} \) are available for several species of wood and wood pellets, as well as a range of agricultural products [15–19, 193, 197]. As stated above (section 6.2.2), ‘solid’ here refers to particle cut from whole biomass on a micrometer to centimeter scale – as opposed to e.g. the distinction between cell wall and micropores made by some authors.

Estimated, averaged values are used in the model calculations, that neglect structural influences such as inhomogeneities and anisotropy, as well as process conditions such as temperature and degree of conversion. Conversion is generally low up to ignition (compare Chapter 5), and influences on material properties are therefore neglected. Change of thermal conductivity and specific heat capacity with conversion appears to be non-linear (e.g., [18, 197, 200]). This may be relevant when burnout of the sample is considered.

Uncertainties in estimating parameters for practical calculations can be reduced by taking into account that thermal conductivity \( \lambda_s \) and solid density \( \rho_s \) are linearly correlated for wood of different species [17, 201, 202]. Specific heat capacity of biomass was found to be independent of particle struc-
ture, and independent of [193] or only mildly dependent [197] on biomass species. Thermal conductivity [16, 18, 193, 196] and specific heat capacity [16, 193, 196, 197] both increase linearly with temperature. Comparing data measured for temperatures within 300–350 K [16, 196, 197], both values appear to increase with a factor of about 1.1–1.2 in this range. In the differential equation describing the temperature field (eq. 6.8), thermal conductivity and specific heat capacity appear in the thermal diffusivity as $a = \lambda/(\rho c_p)$, so that the effects of increasing temperature approximately cancel.

Numerically, the effect of increasing $\lambda_\delta$ is to increase the rate at which heat is internally dissipated. The effective thermal conductivity however only partially depends on the thermal conductivity of the solid (eq. 6.20 and 6.22): Heat conduction in porous media is due to conduction in solid and gas, as well as radiation across void spaces [188]. In terms of temperature sensitivity of the bulk solid, the parameter $K_\varepsilon$ becomes more important. Its estimation involves considerable uncertainty: In [185], a relatively broad range from $K_\varepsilon = 10^{-5}$–$10^{-2}$ m is used, in [145], the range is narrower ($K_\varepsilon = 10^{-4}$–$10^{-3}$ m). On the other hand, in micropores, radiation is found negligible below 1000 K [200].

Permeability $\kappa$ of biomass dust accumulations is not well researched [178]. Pressure drop per unit depth versus gas flow velocities have been measured for various agricultural products [203], and permeabilities could in principle be calculated from such data. There is however considerable scatter: for the same velocity, pressure drop for different materials spans two orders of magnitude. Aganetti et al. [178] suggest a range of $\kappa = 10^{-11}$–$10^{-7}$ m$^2$. Lauttenberger [185] performed model calculations on values $\kappa = 10^{-12}$–$10^{-8}$ m$^2$, which led to overpressures in the sample of 1 kPa for low permeability and 0.1 Pa for high permeability.

**6.3. Results and discussion**

The modelling study consisted of four steps: in step one, the model was tested for plausibility (verification). In the second step, the model was checked against experimental data (validation). In a third step, sensitivity to various modelling parameters was investigated. In the fourth step, a parametric study was carried out to predict the influence of ambient and operating conditions (e.g., sample size and ambient oxygen concentration). Steps 1–3 were based on the geometry, sample size and ambient conditions used in the lab scale fixed bed experiments (Chapter 5).

The model was tested both for static and dynamic heating boundary conditions. In the static cases, temperatures of walls and gas inlet were equal
and constant in time. The solid was initially at the same temperature as its surroundings. Simulations were evaluated by whether or not self-ignition would occur from a given initial temperature. The critical temperature $T_{\text{crit}}$ which led to ignition was determined within $\pm 0.5\,\text{K}$. Idealized boundary and initial conditions were used in static simulations (dry samples, round values for bulk density and oxygen concentration, etc.).

Dynamic heating was applied to simulate the experiments carried out previously. In this case, initial temperatures were set to their measured values. Gas inlet temperatures were kept constant, while the wall temperature was gradually increased, following the measured oven temperature. Boundary and initial conditions (oven wall temperatures, oxygen volume fraction at the oven inlet and initial sample mass) were taken from experimental data. A simulation result was treated as ignition/thermal runaway, if the temperature in the sample increased by more than 60 K compared to the surrounding temperature. The oven temperature at which this occurred is referred to as ignition temperature $T_{\text{ign}}$ in the following. Since the value of $T_{\text{ign}}$ depends on the heating rate, the time to reach ignition ($t_{\text{ign}}$) was additionally evaluated. The 60 K threshold was adapted from EN 15188 [50], where it is valid for isothermal oven tests. Given the runaway behavior of igniting samples, it is assumed that $T_{\text{ign}}$ may be slightly, but not significantly larger than $T_{\text{crit}}$. For very low external heating rates, $T_{\text{ign}}$ approaches $T_{\text{crit}}$.

### 6.3.1. Model verification

The geometry of the bulk solid was modelled as an ideal cylinder (0.03 m diameter, 0.15 m length). For the static simulations, idealized boundary and initial conditions (dry sample, bulk density 120 kg m$^{-3}$, i.e. $m_0 = 12.7\,\text{g}$, 20.0% oxygen, gas flow rate 2.5 L min$^{-1}$) were used. Boundary and initial conditions (wall temperature, gas flow rate, oxygen concentration, sample mass) for the dynamic simulations in the grid refinement study were taken from an experiment on 12.9 g pine, heated at 1 K min$^{-1}$ to 573 K in 19.7% oxygen atmosphere with 2.5 L min$^{-1}$ gas flow rate (at standard conditions). The sample moisture was estimated to be 5% by mass. The solid was discretized in the radial dimension into cylinder shells of equal wall thickness. Grids of 5, 10, 20, 50, and 100 cells were tested. Calculations on finer grids had a slightly shorter time to ignition (for calculations with dynamic wall temperature boundary conditions) and lower critical temperatures for ignition (in isothermal calculations). Results from a grid-refinement study are summarized in Table 6.5. The 50-cell grid was seen as sufficiently accurate, and used in all further simulations.
Table 6.5.: Grid refinement study: pine (model I), 20% oxygen. Material properties are base case values (Table 6.4). Dynamic simulations: 1 K min\(^{-1}\) heating rate to 573 K (nominal values).

<table>
<thead>
<tr>
<th>Cells</th>
<th>static: (T_{\text{crit}}) [K]</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dynamic: (T_{\text{ign}}) [K]</td>
<td>481.5</td>
<td>480.0</td>
<td>479.5</td>
<td>479.0</td>
<td>479.0</td>
<td>479.0</td>
</tr>
<tr>
<td>dynamic: (t_{\text{ign}}) [s]</td>
<td>494.1</td>
<td>493.5</td>
<td>493.3</td>
<td>493.0</td>
<td>493.0</td>
<td>493.0</td>
</tr>
</tbody>
</table>
|        | 11808.3 | 11778.4 | 11764.7 | 11753.3 | 11750.5 |}

Radial profiles of temperature, oxygen concentration and sample bulk density show a characteristic behavior at thermal runaway (Fig. 6.4). Results shown are from the 50-cell simulation of the dynamic grid refinement study. Radial profiles were sampled as the center cell reached 450 K, and then in 50 K-intervals to 800 K. Temperatures increase rapidly after the center reaches 600 K (11766 s). Up to about 500 K, radial gradients are very small (Fig. 6.4a). Temperatures then rapidly increase in the center of the geometry, but only slowly on the outside. Oxygen volume fraction (Fig. 6.4b) initially decreases nearly homogeneously across the cylinder radius. Gas mixing is fast enough to even out most local concentration differences for \(<11767\) s (center temperature \(\leq 650\) K). Oxygen diffusion limitations lead to a radial gradient as the reaction progresses. These transport limitations are apparent from 11767 s onward (center temperature \(\geq 700\) K). Bulk density profiles (Fig. 6.4c) appear as the inverted form of the temperature distribution. The sample is ‘hollowed out’ as temperatures increase in the center.

Heat and mass transfer limitations are largest at locations farthest away from the solid surface. Ignition in a hot spot is characteristic of heat transfer limited situations [48,57]. This type of behavior was expected based on experimental observations (see Chapter 5). Qualitatively similar results are reported by other researchers [65,105,120,173,177]. In (partially) mass transfer limited situations, the hot spot can be closer to the outer sample surface [175,178]. For the configuration used in the experiments and for model validation, it was however estimated that mass transfer limitations do not influence ignition onset (Chapter 5.3). Modelling results are in agreement with this estimate (Figs. 6.4a and 6.4b).

### 6.3.2. Model validation

The model was compared to supercritical (sample undergoes thermal runaway), subcritical (sample shows mild self-heating) and pyrolysis experiments for validation. Measured oven temperatures and oxygen inlet concentrations
Figure 6.4.: Simulated radial distributions of temperature, oxygen and density around thermal runaway. Pine, model I; boundary conditions: 20% oxygen atmosphere, heating at 1 K min\(^{-1}\) to 573 K (nominal conditions)
were used as boundary and initial conditions. Similar to the experiments, model calculations were carried out for various boundary conditions. The aim was to determine which combination of parameters would lead to ignition, with the critical ambient temperature as the most important parameter. Generally, the model tended to predict self-ignition at lower (oven) temperatures than were observed experimentally.

6.3.2.1. Qualitative comparison

Comparison of model and experiment for four different materials is shown in Figures 6.5 and 6.6. Differences between the two oxidation models were negligible for practical purposes. Agreement between model and experiment differed among the materials tested. Predictions of ignition onset were best for pine and sunflower. For sunflower, the induction phase observed experimentally (between 120–150 min – compare also data in Appendix A.3.7.5) was however not seen in the model. Corresponding modelled CO and CO\(_2\) emissions are found in Appendix A.6. As reaction rates and oxygen consumption are low until the onset of ignition (Fig. 6.6), the off-gas model only has weak influence on the onset of ignition.

Quality of model predictions tended to deteriorate once ignition was reached: temperatures in the sample center increased much faster in the simulations than in the experiments. Similar overly sharp temperature gradients have also been reported by other researchers [178, 181]. It appears that reaction rates are overpredicted, or that dampening effects are underpredicted (oxygen diffusion limitations, thermal conductivity, heat absorption), or both. Possible explanations are that the kinetic mechanism is not valid for high temperatures (>550 K) and heating rates (>5 K min\(^{-1}\)). Agreement between both kinetic models and thermogravimetric data diminished above 600 K (Chapter 4). Uncertainties in kinetic models can be amplified in bench scale simulations [145]. Secondly, diffusion rates were calculated for a fixed reference frame. Product gas release rates however increase drastically at ignition, impeding oxygen access to the reaction zone. The error made by treating counterflow diffusion as stagnant diffusion may be significant for high gas flow rates [204]. Additionally, changes to the biomass structure can influence thermal conductivity [200] or specific heat capacity [197]. Since the purpose of this model is to predict under which conditions ignition occurs, such effects were neglected. Calculations were therefore stopped when thermal runaway was detected.
Figure 6.5.: Modelled and experimental sample center temperatures for beech, pine, sunflower and wheat. Nominal experimental conditions: heating at 1 K min\(^{-1}\) to 573 K in 20% oxygen atmosphere. See Table 5.4 for further experimental data. Corresponding oxygen consumption shown in Fig. 6.6.

### 6.3.2.2. Quantitative comparison

Evaluation of the model was focused on how well ignition temperatures could be predicted. The kinetic model was additionally validated by comparing predicted mass loss with measured values for subcritical experiments and pyrolysis experiments. A distinction was made between the type of experiment to be modelled. Experiments such as those in Fig. 6.5 were run with constant oven heating rate throughout the ignition- and most of the burnout phase. In those cases, the measured wall temperatures were used directly as boundary conditions. Other experiments were run at temperatures around the critical ambient temperature (Chapter 5.4.2 and 5.4.3). When measured oven wall temperatures were used as boundary conditions for these simulations, ignition was predicted for cases in which it did not happen in the experiment. A factor \(\tau\) was introduced to dampen the wall temperatures used in such
Figure 6.6.: Modelled and experimental bulk gas oxygen concentrations for beech, pine, sunflower and wheat. Compare Fig. 6.5.

Simulations. The proportionality factor is defined by the following equation:

\[
T_{w,\text{sim}}(t) = \tau \cdot T_{w,\text{exp}}(t)
\]  

(6.30)

Values of \( \tau \) were determined individually for each model run, and were within the range of \( 0.94 \leq \tau \leq 1 \). An example of this dampening is seen in Figures 6.7 and 6.8. Experimentally, heating the oven to 501 K did not result in thermal runaway (Fig. 6.7), while using a final wall boundary temperature of 485 K led to ignition in the model (Fig. 6.8). Relative errors \( \delta_T \) and \( \delta_m \) were defined to compare experiments and simulations:

\[
\delta_T = \frac{T_{\text{ign, sim}} - T_{\text{ign, exp}}}{T_{\text{ign, exp}}}
\]  

(6.31)

\[
\delta_m = \frac{\Delta m_{\text{sim}} - \Delta m_{\text{exp}}}{\Delta m_{\text{exp}}}; \quad \Delta m = m_0 - m_f
\]  

(6.32)

Results for several supercritical simulations are summarized in Table 6.6. Relative errors \( \delta_T \) of \( T_{\text{ign}} \) were between \(-5.5\% \) and \(-1\% \) (corresponding to temperature differences of 5–27 K between model and experiment). Model
Figure 6.7.: Comparison of subcritical experiment and simulation. Experimental parameters: Pine, 20% oxygen, nominal heating rate 1 K min$^{-1}$ to 501 K. Modelling: pine (model I), $\tau = 0.96$ ($T_{w,f,\text{sim}} = 481$ K). Material properties are base case values (Table 6.4).

Figure 6.8.: Comparison of supercritical experiment and simulation. Experimental parameters: Pine, 20% oxygen, nominal heating rate 1 K min$^{-1}$ to 506 K. Modelling: pine (model I), $\tau = 0.96$ ($T_{w,f,\text{sim}} = 485$ K). Material properties are base case values (Table 6.4).
Table 6.6: Ignition temperature model validation: relative errors $\delta T$ are within $-1\%$ to $-5.5\%$.

Boundary and initial conditions were taken from experimental data. Simulations in the top part of the table correspond to Fig. 6.5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Model I</th>
<th>Model II</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.5</td>
<td>1</td>
<td>5.2</td>
<td>47.5</td>
</tr>
<tr>
<td>47.9</td>
<td>1</td>
<td>5.2</td>
<td>47.5</td>
</tr>
<tr>
<td>47.2</td>
<td>1</td>
<td>5.2</td>
<td>47.5</td>
</tr>
<tr>
<td>47.9</td>
<td>1</td>
<td>5.2</td>
<td>47.5</td>
</tr>
</tbody>
</table>

Abbreviations: c = coarse (600-1000 µm particles), f = fine (50-200 µm particles). Conditions were taken from experimental data. Simulations in the top part of the table correspond to Fig. 6.5.
II performed slightly better than model I. Deviations were largest for wheat and simulations in 8% oxygen atmosphere (pine). Good agreement between model and experiment were seen for sunflower and pine in 20% oxygen atmosphere. As the model resulted in systematically lower ignition temperatures $T_{\text{ign}}$, predictions err on the safe side.

Simulations of subcritical oxidation experiments and pyrolysis experiments were used to validate the mass loss predicted by the model, Table 6.7. As discussed above, the wall boundary condition $T_{w,\text{sim}}$ was lowered compared to the measured temperature $T_{w,\text{exp}}$ to prevent ignition in the subcritical simulations. Values of $\tau$ were between 0.94–0.96 for model I and within 0.97–0.95 for model II. The simulations predicted lower mass loss (i.e., higher residual masses) in all oxidation cases (Table 6.7). Prediction errors were within 0.5–2.3 g, corresponding to a relative error of $\delta_m = 11–52\%$. In this case, model I resulted in better predictions than model II. The comparatively large relative errors may be due to lowering the wall temperatures in the simulations. Interestingly, though, errors $\delta_m$ did not appear to correlate with the dampening factor $\tau$ or the total duration of experiment and simulation ($t_f$).

The pyrolysis simulations compared more favorably to their respective experiments (bottom part of Table 6.7). Mass loss was slightly (7–15%) over-predicted in the model.

In conclusion of model verification and validation, model predictions were plausible and in fair agreement with experimental data, especially given that the modelling parameters were developed independently of the lab-scale experiments. The central aim of the model was to predict temperatures at which ignition would occur, and this could be done with reasonable accuracy.

### 6.3.3. Parameter sensitivity

An analysis of the parametric sensitivity was carried out for both static and dynamic oven temperature boundary conditions. The former is more interesting when using the model to predict critical temperatures $T_{\text{crit}}$. The dynamic case was included to evaluate whether the differences between model and validation experiment could be attributed to the choice of modelling parameters. The two cases which had previously been used in the grid refinement study were used as the base cases in the sensitivity analysis (pine, model I, dry sample, 20.0% oxygen, bulk density 120 kg m$^{-3}$ for the static boundary conditions; and pine, model I, heated at 1 K min$^{-1}$ to 573 K in 19.7% oxygen atmosphere, 12.9 g sample mass for the dynamic boundary conditions). The sensitivity analysis was run by varying one parameter at a
Table 6.7: Mass loss model validation for subcritical oxidation and pyrolysis.

\[
\Delta m = m_0 - m_f
\]

is predicted too low in oxidation experiments and too high in pyrolysis experiments. Oventemperatures used as boundary condition had to be lowered (\(\tau < 1\)) to prevent ignition in subcritical simulations. Pyrolysis kinetics are the same for both model I and II (lower part of the table).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>T w, f</th>
<th>(O_2), %</th>
<th>(t_f), min</th>
<th>(m_0), g</th>
<th>(\Delta m), g</th>
<th>(\tau)</th>
<th>(\Delta m), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine (f)</td>
<td>Pine (f)</td>
<td>500</td>
<td>19.5</td>
<td>417.8</td>
<td>0.05</td>
<td>1.097</td>
<td>0.38</td>
<td>0.97</td>
</tr>
<tr>
<td>Pine (f)</td>
<td>Pine (f)</td>
<td>502</td>
<td>19.6</td>
<td>359.1</td>
<td>10.01</td>
<td>2.39</td>
<td>0.62</td>
<td>0.96</td>
</tr>
<tr>
<td>Pine (f)</td>
<td>Pine (f)</td>
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<td>19.7</td>
<td>948.1</td>
<td>14.99</td>
<td>4.85</td>
<td>0.96</td>
<td>0.44</td>
</tr>
<tr>
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<td>Pine (f)</td>
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<td>19.6</td>
<td>948.1</td>
<td>14.99</td>
<td>4.85</td>
<td>0.96</td>
<td>0.44</td>
</tr>
<tr>
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<td>Pine (f)</td>
<td>501</td>
<td>19.7</td>
<td>431.4</td>
<td>8.05</td>
<td>1.97</td>
<td>0.58</td>
<td>0.32</td>
</tr>
<tr>
<td>Beech</td>
<td>Pine (f)</td>
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<td>7.9</td>
<td>321.4</td>
<td>18.00</td>
<td>2.69</td>
<td>0.95</td>
<td>3.27</td>
</tr>
<tr>
<td>Pine (c)</td>
<td>Pine (f)</td>
<td>512</td>
<td>8.1</td>
<td>432.1</td>
<td>19.49</td>
<td>4.17</td>
<td>0.95</td>
<td>3.05</td>
</tr>
<tr>
<td>Pine (c)</td>
<td>Pine (f)</td>
<td>512</td>
<td>8.1</td>
<td>432.1</td>
<td>19.49</td>
<td>4.17</td>
<td>0.95</td>
<td>3.05</td>
</tr>
<tr>
<td>Pine (c)</td>
<td>Pine (f)</td>
<td>512</td>
<td>8.1</td>
<td>432.1</td>
<td>19.49</td>
<td>4.17</td>
<td>0.95</td>
<td>3.05</td>
</tr>
<tr>
<td>Sunflower</td>
<td>Sunflower</td>
<td>581</td>
<td>0</td>
<td>348.4</td>
<td>40.00</td>
<td>7.02</td>
<td>0.97</td>
<td>2.41</td>
</tr>
<tr>
<td>Wheat</td>
<td>Wheat</td>
<td>580</td>
<td>0</td>
<td>348.4</td>
<td>40.00</td>
<td>7.02</td>
<td>0.97</td>
<td>2.41</td>
</tr>
</tbody>
</table>

Abbreviations: c = coarse (600–1000 µm particles), f = fine (50–200 µm particles). For both models I and II, the same trend for subcritical oxidation and pyrolysis is observed. Lower temperatures used as boundary condition had to be lowered (\(\tau < 1\)) to prevent ignition in subcritical simulations. Pyrolysis kinetics are the same for both model I and II (lower part of the table). See text for discussion.
time, keeping the others at the values defined for the base case calculations.

### 6.3.3.1. Sensitivity to material properties

Material properties were varied within boundaries found in the literature (compare Table 6.4), as well as by ±10 %, ±25 % and ±50 % around the base case values. Results from the sensitivity analysis of the material properties are listed in Tables 6.8 (static boundary conditions) and 6.9 (dynamic boundary conditions). For the dynamic boundary conditions, ignition temperatures $T_{\text{ign}}$ are listed for comparison.

Relatively large effects are seen for parameters influencing the heat balance, especially thermal conductivity $\lambda_s$, density $\rho_s$, and the coefficient for radiative heat transfer in a porous solid $K_\varepsilon$. Values within 0.1–0.6 W m$^{-1}$K$^{-1}$ and 600–1000 kg m$^{-3}$ could both change the critical temperature for ignition within an interval of 7.5 K. In the dynamic case, time to ignition varied within 211 s (thermal conductivity) and 230 s (density). Varying $K_\varepsilon$ within $10^{-5}$–$10^{-2}$ m [185] gave an interval of 8 K for critical temperatures, and 257 s for time to ignition in the example tested. Larger values of $\lambda_s$ and $K_\varepsilon$ increased the thermal diffusivity, acting against ignition. Larger solid densities (at constant bulk density $\rho_{\text{tot}} = 120$ kg m$^{-3}$) had the opposite effect (lowering the effective thermal conductivity for constant $\lambda_s$ via larger $\phi$). Effects of varying thermal conductivity and solid density cancelled, when the relation $\lambda_s \propto \rho_s$ was respected (compare section 6.2.3): Varying thermal conductivity and solid density simultaneously within ±50 % had little or no effect on critical temperatures ($\Delta T = 1$ K) or time to ignition ($\Delta t = 15$ s).

The specific heat capacity of the solid $c_{p,s}$ had an effect on the dynamics of the system (delay time for thermal runaway) but only mildly influenced the critical temperature within the range tested. Some influences of sample emissivity on critical temperature (ranges: $\Delta T = 3.5$ K, $\Delta t = 65$ s) were observed, indicating that enhanced external heat dissipation can inhibit or delay self-ignition. Wall emissivity, sample permeability and diffusion coefficient at reference temperature did not have a notable effect on simulation predictions within the range of values investigated.

In summary, both internal and external heat transfer appear to have an effect on thermal runaway, while influence of mass transfer limitations on the onset of thermal runaway are low. As discussed above, those limitations likely become relevant once reaction rates accelerate.
<table>
<thead>
<tr>
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<th>Value</th>
<th>Value</th>
</tr>
</thead>
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<tr>
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<td>+%</td>
<td>-%</td>
<td>max</td>
<td>min</td>
<td>base value</td>
</tr>
<tr>
<td>-</td>
<td>+25%</td>
<td>%</td>
<td>+10%</td>
<td>%</td>
<td>+50%</td>
</tr>
<tr>
<td>-</td>
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<td>%</td>
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<td>%</td>
<td></td>
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<tr>
<td>-</td>
<td>+5%</td>
<td>%</td>
<td></td>
<td>-%</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>+1%</td>
<td>%</td>
<td></td>
<td>-1%</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>-1%</td>
<td>%</td>
<td></td>
<td>-2%</td>
<td></td>
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<tr>
<td>-</td>
<td>-2%</td>
<td>%</td>
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<td>-5%</td>
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<td>%</td>
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<td>%</td>
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<td>-25%</td>
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</tr>
<tr>
<td>-</td>
<td>-25%</td>
<td>%</td>
<td></td>
<td>-50%</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.8: Material parameters sensitivity analysis for static temperature boundary conditions. Critical temperature for pine, model I, dry sample, 2.0% oxygen, bulk density 120 kg m⁻³. The Critical temperature for the base case parameters were varied individually, one at a time. All simulations run for 1 day.
Table 6.9.: Material parameters sensitivity analysis for dynamic temperature boundary conditions. Ignition occurs for \( T_{\text{ign}} = 493.0 \text{K} \) at \( t_{\text{ign}} = 11753.3 \text{s} \) in the base case. Parameters were varied individually, one at a time. All simulations run for pine, model I, heated at 1 K min\(^{-1}\) to 573 K in 19.7% oxygen atmosphere, 12.9 g sample mass.

<table>
<thead>
<tr>
<th>parameter [units]</th>
<th>spread within parameter range</th>
<th>variation around base case value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>base value</td>
<td>min</td>
</tr>
<tr>
<td>( \lambda ) [W m(^{-1}) K(^{-1})]</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>( \Delta t_{\text{ign}} ) [s]</td>
<td>-62.9</td>
<td>148</td>
</tr>
<tr>
<td>( \Delta T_{\text{ign}} ) [K]</td>
<td>-1.2</td>
<td>2.8</td>
</tr>
<tr>
<td>( \rho ) [kg m(^{-3})]</td>
<td>600</td>
<td>200</td>
</tr>
<tr>
<td>( \Delta t_{\text{ign}} ) [s]</td>
<td>188</td>
<td>-41.6</td>
</tr>
<tr>
<td>( \Delta T_{\text{ign}} ) [K]</td>
<td>3.5</td>
<td>-0.8</td>
</tr>
<tr>
<td>( c_{p,s} ) [J kg(^{-1}) K(^{-1})]</td>
<td>2000</td>
<td>1100</td>
</tr>
<tr>
<td>( \Delta t_{\text{ign}} ) [s]</td>
<td>-247</td>
<td>26.3</td>
</tr>
<tr>
<td>( \Delta T_{\text{ign}} ) [K]</td>
<td>-4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>( K ) [m]</td>
<td>10(^{-3})</td>
<td>10(^{-5})</td>
</tr>
<tr>
<td>( \Delta t_{\text{ign}} ) [s]</td>
<td>-31.4</td>
<td>225</td>
</tr>
<tr>
<td>( \Delta T_{\text{ign}} ) [K]</td>
<td>-0.6</td>
<td>4.3</td>
</tr>
<tr>
<td>( \varepsilon_s ) [-]</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>( \Delta t_{\text{ign}} ) [s]</td>
<td>-53.8</td>
<td>11.3</td>
</tr>
<tr>
<td>( \Delta T_{\text{ign}} ) [K]</td>
<td>-1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \varepsilon_w ) [-]</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>( \Delta t_{\text{ign}} ) [s]</td>
<td>-2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>( \Delta T_{\text{ign}} ) [K]</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( D_{\text{ref}} ) [m(^2) s(^{-1})]</td>
<td>1.5 \times 10(^{-5})</td>
<td>1.3 \times 10(^{-5})</td>
</tr>
<tr>
<td>( \Delta t ) [s]</td>
<td>2.0</td>
<td>-4.3</td>
</tr>
<tr>
<td>( \Delta T ) [K]</td>
<td>0</td>
<td>-0.1</td>
</tr>
<tr>
<td>( \kappa ) [m(^2)]</td>
<td>10(^{-10})</td>
<td>10(^{-12})</td>
</tr>
<tr>
<td>( \Delta t_{\text{ign}} ) [s]</td>
<td>-2.2</td>
<td>23.6</td>
</tr>
<tr>
<td>( \Delta T_{\text{ign}} ) [K]</td>
<td>0</td>
<td>0.4</td>
</tr>
</tbody>
</table>
6.3.3.2. Sensitivity to reaction mechanism parameters

The influence of reaction rate constants $k$ as well as parameters $\gamma_{CO}/\gamma_{CO_2}$ and of the lower heating value $h_{LHV}$ were investigated in the same manner as the material properties. In this part of the study, uniform ratios $\gamma_{CO}/\gamma_{CO_2}$ were used instead of the component specific values listed in Table 6.3. The range of 0.2–0.8 was loosely based on the fixed bed experiments (compare Appendix A.3.7.5). Reaction rates were varied by modifying the pre-exponential factor $k_0$ of the oxidation reaction of the volatilizable fraction (compare section 6.2.3) by ±10%, ±25% and ±50%. Critical temperatures $T_{crit}$ and time to ignition $t_{ign}$ were very sensitive to the rate constants (via the pre-exponential factors $k_0$) and the lower heating value $h_{LHV}$, Tables 6.11 and 6.10. This is especially apparent in comparison to the sensitivity to material properties, Tables 6.8 (static boundary conditions) and 6.9 (dynamic boundary conditions).

The split between CO and CO$_2$ affects the stoichiometric oxygen demand. It may also have an effect (<10%) on the estimated heat of reaction (compare section 6.2.3). This is however treated separately by modifying $h_{LHV}$ (see below). The value assumed for $\gamma_{CO}/\gamma_{CO_2}$ had negligible influence on both the critical ignition temperature (Table 6.10) as well as on the ignition delay (Table 6.11).

In contrast, varying the heat of reaction by assuming different values for $\Delta h_{LHV}$ had large effects on thermal runaway. In practice, it is more probable that the net heat of reaction is lower than that estimated by the lower heating value (which assumes complete conversion of the fuel). Critical ignition temperatures could then be in the order of 1–10 K higher for the isothermal example calculations (Table 6.10). Ignition could be delayed in the order of several minutes in the dynamic simulations (Table 6.11).

Kinetic parameters can normally be fit with minimal numerical error to thermogravimetric data (compare Chapter 4). To quantify scaling effects, the influence of reaction rate constants was investigated further. Critical temperatures for each species were determined, based on the species’ composition and reaction mechanism (model I), but using the same material properties and sample size in all simulations (bulk density 120 kg m$^{-3}$, 20% oxygen atmosphere, base case values for material properties – Table 6.4). A relatively large spread in critical temperatures, $\Delta T = 20$ K, was seen, were the critical temperature is the lowest temperature for which thermal runaway would occur in isothermal simulations (Table 6.12, top section). In a the next step, hybrid reaction mechanisms were created: Composition (both in terms of elements and biomass components), heating value and pyrolysis mechanism were fixed to values representing pine (compare Tables 4.2, 4.3 and 6.2), and
Table 6.10.: Reaction mechanism sensitivity analysis for static temperature boundary conditions. Critical temperature $T_{\text{crit}}$ is 479 K for the base case. All simulations run for pine, model I, dry sample, 20.0% oxygen, bulk density 120 kg m$^{-3}$. Compare sensitivity to material properties in Table 6.8.

<table>
<thead>
<tr>
<th>parameter [units]</th>
<th>spread within parameter range</th>
<th>variation around base case value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$ [s$^{-1}$]</td>
<td>$1.04 \times 10^7$</td>
<td>-10% 25% -50% +10% +25% +50%</td>
</tr>
<tr>
<td>$\Delta T_{\text{crit}}$ [K]</td>
<td>- -</td>
<td>9.36 x 10^6 7.80 x 10^6 5.20 x 10^6 1.14 x 10^7 1.30 x 10^7 1.56 x 10^7</td>
</tr>
<tr>
<td>$\gamma_{\text{CO}}/\gamma_{\text{CO}_2}$ [-]</td>
<td>0.5 0.2 0.8</td>
<td>0.45 0.375 0.25 0.55 0.625 0.75</td>
</tr>
<tr>
<td>$\Delta T_{\text{ign}}$ [K]</td>
<td>- -</td>
<td>- - - - - -</td>
</tr>
<tr>
<td>$h_{\text{LHV}}$ [MJ kg$^{-1}$]</td>
<td>19.80</td>
<td>- -</td>
</tr>
<tr>
<td>$\Delta T_{\text{ign}}$ [K]</td>
<td>- -</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.11.: Reaction mechanism sensitivity analysis for dynamic temperature boundary conditions. Ignition occurs for $T_{\text{ign}} = 493.0$ K at $t_{\text{ign}} = 11753.3$ s in the base case. All simulations run for pine, model I, heated at 1 K min$^{-1}$ to 573 K in 19.7% oxygen atmosphere, 12.9 g sample mass. Compare sensitivity to material properties in Table 6.9.

<table>
<thead>
<tr>
<th>parameter [units]</th>
<th>spread within parameter range</th>
<th>variation around base case value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$ [s$^{-1}$]</td>
<td>$1.04 \times 10^7$</td>
<td>-10% 25% -50% +10% +25% +50%</td>
</tr>
<tr>
<td>$\Delta t_{\text{ign}}$ [s]</td>
<td>- -</td>
<td>9.36 x 10^6 7.80 x 10^6 5.20 x 10^6 1.14 x 10^7 1.30 x 10^7 1.56 x 10^7</td>
</tr>
<tr>
<td>$\Delta T_{\text{ign}}$ [K]</td>
<td>- -</td>
<td>94.2 260 628 -85.4 -201 -363</td>
</tr>
<tr>
<td>$\gamma_{\text{CO}}/\gamma_{\text{CO}_2}$ [-]</td>
<td>0.5 0.2 0.8</td>
<td>0.45 0.375 0.25 0.55 0.625 0.75</td>
</tr>
<tr>
<td>$\Delta t_{\text{ign}}$ [s]</td>
<td>- -</td>
<td>-0.2 -0.5 -1.0 0.2 0.4 0.8</td>
</tr>
<tr>
<td>$\Delta T_{\text{ign}}$ [K]</td>
<td>0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>$h_{\text{LHV}}$ [MJ kg$^{-1}$]</td>
<td>19.80</td>
<td>- -</td>
</tr>
<tr>
<td>$\Delta t_{\text{ign}}$ [s]</td>
<td>- -</td>
<td></td>
</tr>
<tr>
<td>$\Delta T_{\text{ign}}$ [K]</td>
<td>- -</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.12.: Sensitivity to kinetic parameters for mechanism derived from thermogravimetric analysis (top part), and ‘hybrid’ mechanisms created for numerical experiments (middle and bottom). See text for discussion. Data for the pyrolysis mechanism is found in Table 4.3, composition information is in Table 6.2 (elements) and 4.2 (components). Abbreviations: b = beech, p = pine, s = sunflower, w = wheat.

<table>
<thead>
<tr>
<th>oxidation ( (E_a = 130, \text{kJ mol}^{-1}) )</th>
<th>pyrolysis</th>
<th>composition</th>
<th>( h_{\text{LHV}} )</th>
<th>( T_{\text{crit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_0 ) [s(^{-1})]</td>
<td>( \nu_s )</td>
<td>( \nu_{O_2} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.00 \times 10^7</td>
<td>2.2</td>
<td>0.45</td>
<td>(b) beech</td>
<td>beech</td>
</tr>
<tr>
<td>1.04 \times 10^7</td>
<td>1.25</td>
<td>0.4</td>
<td>(p) pine</td>
<td>pine</td>
</tr>
<tr>
<td>1.62 \times 10^7</td>
<td>2.5</td>
<td>0.5</td>
<td>(s) sunflower</td>
<td>sunflower</td>
</tr>
<tr>
<td>1.49 \times 10^7</td>
<td>1.6</td>
<td>0.5</td>
<td>(w) wheat</td>
<td>wheat</td>
</tr>
</tbody>
</table>

| \( k_0 \) [s\(^{-1}\)] | \( \nu_s \) | \( \nu_{O_2} \) | | |
| 2.00 \times 10^7 | 2.2 | 0.45 | (b) pine | pine | 19.8 (p) | 461.5 |
| 1.62 \times 10^7 | 2.5 | 0.5 | (s) pine | pine | 19.8 (p) | 457.5 |
| 1.49 \times 10^7 | 1.6 | 0.5 | (w) pine | pine | 19.8 (p) | 458 |

| \( 1.04 \times 10^7 \) | 1.25 | 0.4 | (p) none | pine | 19.8 (p) | 478.5 |

combined with the rate expressions for oxidation of beech, sunflower husk pellets and wheat straw, respectively. The overall trends were the same as when the ‘correct’ mechanism was applied, Table 6.12 (middle section).

This suggests that the differences seen between biomasses in Figs. 6.5 and 6.6 are largely due to the different oxidation kinetics. Composition generally does not vary much among biomasses. Variations of the lower heating value vary within ±6% around their mean, which would account only for minor variations in the critical temperature (compare Table 6.8). Comparing the critical temperatures for the two cases with sunflower oxidation kinetics, it also appears that the higher value of the lower heating value (20.5 MJ kg\(^{-1}\) vs. 19.8 MJ kg\(^{-1}\)) is compensated by a much higher ash content (5.2% vs. 0.3%) – i.e., a lower amount of reactive organic content at equal solid mass (compare Table 4.2).

The pyrolysis mechanism appears to have only a minor role in predicting critical temperatures. For the mechanism which consists only of parallel steps, pyrolysis reactions may inhibit thermal runaway by competing for reactive material with oxidation reactions; and promote thermal runaway by reducing the density (and thus heat capacity \( m \cdot c_p \)). Conversion of the solid is however low until the onset of thermal runaway. Setting the reaction rates of pyrolysis to zero (Table 6.12, bottom) had only little effect on the critical temperature \( (\Delta T = -0.5\, \text{K}) \).

Kinetic parameters \( k_0 \) and \( E_a \) are highly coupled, and different parameter couples can give similar reaction rate constants \( k \), if the temperature in-
interval is sufficiently small. In the second part of the kinetic parameters sensitivity analysis, $k(T)$ of the oxidation reaction was therefore varied by choosing different sets of $k_0$ and $E_a$, so that rates are equal at $T = 470\,\text{K}$ (Fig. 6.9). Changing the kinetic parameters had a profound effect on both the time to ignition (dynamic simulations), as well as the critical temperature for ignition (isothermal simulations), Table 6.13. Predicted critical temperatures increased exponentially with decreasing activation energy (Table 6.13). Lowering the activation energy between $70-130\,\text{kJ}\cdot\text{mol}^{-1}$ also increased the delay time until rapid reactions are reached (Figure 6.10) and the time to ignition (Table 6.13) in dynamic simulation. The kinetic parameters with $E_a = 60\,\text{kJ}\cdot\text{mol}^{-1}$ did not result in ignition for the simulated test case, but only lead to subcritical self-heating. For those cases in which supercritical self-heating was predicted, the induction time increased.

Kinetic parameters were determined in the range $423-523\,\text{K}$ (corresponding to the range $1.91-2.36\,\text{K}^{-1}$ in Fig. 6.9). While rates differ by approximately one order of magnitude between the parameter sets at the edges of that interval, they are much lower than the corresponding pyrolysis rates in the same temperature range ($10^{-6}-10^{-4}$ for pyrolysis vs. $10^{-10}-10^{-6}$ for oxidation - compare Chapter 4).

![Figure 6.9.: Arrhenius plot for kinetic parameter sets. New sets of kinetic parameters were created to assess the sensitivity towards activation energy of oxidation reactions. Values listed in Table 6.13.](image)
Table 6.13.: Model sensitivity towards activation energy of the oxidation reaction. Kinetic parameters were developed based on equal rates at 470K, compare Fig. 6.9. Reaction orders \( \nu_s = 1.25 \) (solid conversion) and \( \nu_{O_2} = 0.4 \) (oxygen). Base case values: \( \Delta T_{\text{crit}} = 479 \text{K}, \Delta T_{\text{ign}} = 493 \text{K}, \Delta t_{\text{ign}} = 11753 \text{s} \).

<table>
<thead>
<tr>
<th>( E_a ) [kJ mol(^{-1})]</th>
<th>( k_0 ) [s(^{-1})]</th>
<th>static ( \Delta T_{\text{crit}} ) [K]</th>
<th>static ( \Delta T_{\text{ign}} ) [K]</th>
<th>static ( \Delta t_{\text{ign}} ) [s]</th>
<th>dynamic ( \Delta T_{\text{ign}} ) [K]</th>
<th>dynamic ( \Delta t_{\text{ign}} ) [s]</th>
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<tr>
<td>130</td>
<td>( 1.04 \times 10^7 )</td>
<td>0</td>
<td>0</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>( 8.05 \times 10^5 )</td>
<td>2.5</td>
<td>2.9</td>
<td>157</td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>( 6.23 \times 10^4 )</td>
<td>6.0</td>
<td>6.8</td>
<td>351</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>( 4.82 \times 10^3 )</td>
<td>10.5</td>
<td>12.0</td>
<td>603</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>( 3.73 \times 10^2 )</td>
<td>17.0</td>
<td>18.6</td>
<td>920</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>( 2.88 \times 10^1 )</td>
<td>27.0</td>
<td>27.7</td>
<td>1367</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>( 2.23 \times 10^0 )</td>
<td>46.0</td>
<td>43.4</td>
<td>2092</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>( 1.73 \times 10^{-1} )</td>
<td>95.5</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.10.: Sample center temperatures for different kinetic parameters. See Table 6.13.
6.3.4. Scaling

Further isothermal simulations were carried out to investigate the effects of sample size, sample mass, bulk density, and ambient oxygen concentration. Effects of sample size were investigated by scaling all geometric lengths of the model by factors of 2, 4, 8 and 16. Gas volumetric flow rates were correspondingly scaled by $2^3$, $4^3$, $8^3$ and $16^3$ in order to keep gas velocities constant (for convective heat transfer). All other parameters were kept constant. Simulations were carried out for pine and sunflower. Critical temperatures for thermal runaway showed an approximately logarithmic decrease with increasing sample size, Fig. 6.11. Critical temperatures dropped by 15–20 K for every doubling of the characteristic lengths (i.e., the sample diameter). The effect was more pronounced for small samples/large temperatures. Differences between the pine model species and the sunflower model gradually decreased with larger sample sizes/lowertemperatures. Dust accumulations with characteristic dimensions (e.g., bed depth) of 0.05–0.1 m could plausibly approach critical conditions for temperatures above 430 K.

Sample mass effects at constant volume were calculated by varying both solid density and bulk density by factors of 0.5, 1.5, 2, 3 and 4; keeping all other parameters constant. The bed porosity remained at a constant value of $\phi = 0.8$. Calculations showed a logarithmic decrease of critical temperatures with increasing sample mass (Fig. 6.12). Similarly, bed compaction was investigated by varying the bulk density a constant solid density. More
compact samples (higher bulk density) had lower critical ignition temperatures. This qualitatively agrees with experimental findings (Chapter 5.4.2): increasing sample bulk densities by a factor of 1.5 could reduce the critical temperature in the order of 5 K. Ambient temperatures were however not varied finely enough in the experiments to draw definite conclusions from this comparison.

The reduced porosity allowed for higher ambient temperatures compared to the case in which a larger sample mass was achieved by a higher solid density. As ignition did not appear to be mass-transfer limited in the simulations, this effect is (numerically) due to a larger effective thermal conductivity (and thus better heat dissipation) in the dust bed for low porosities. The extrapolation should be done with care, however, as some of the modelling assumptions relating to gas transport break down for low bed porosities.

Based on the fixed bed experiments, it was suspected that the structure of the bed has a minor, but noticeable influence on self-heating and spontaneous ignition. Model calculations appear to confirm this, even though the only parameter describing the bed structure is the porosity. Further research in this area may be necessary. In the experiments, it was seen that particles naturally formed beds of widely varying bulk densities, depending both on the material as well as on the particle size fractions. Fibers from wheat straw (200–400 µm) formed beds of ca. 100 kg/m³. Fine pine dusts (50–200 µm) formed beds of ca. 115 kg/m³ and could be manually compacted to 170 kg/m³. The latter value was reached by loose beds of (600–1000 µm).
particles of the same pine wood, and could be increased to 200 kg/m$^3$ by slight compaction (compare Chapter 5.4.2). Ground sunflower husk pellets (125–850 µm) had a natural bulk density of around 380 kg/m$^3$. In practical situations, dust beds are likely formed by a much larger range of particle sizes, from dust grains small enough to pass the classifier to whole or broken pellets. Additionally, solid density of the particles may differ: Densities of biomass pellets are reported within 1100–1350 kg m$^{-3}$ [15–17], which is higher than the values of e.g. raw wood. On the other hand, the compaction effect of pelletization is reversible, as solid- and bulk densities of ground pellet dusts are lower than those of the intact pellets [16].

Simulations were only mildly sensitive to ambient oxygen concentrations, Fig. 6.13. Increase of the critical ambient temperature when ambient oxygen is reduced is less than would be expected, both based on experiments reported in Chapter 5, as well as data published for wood [59] and cork dusts [66]. As described above, agreement between model and experiment was generally better for cases with 20 % oxygen than for 8 % oxygen. Since mass transfer limitations are low, this can likely be traced to the reaction order in oxygen used in the kinetic mechanism.

### 6.4. Conclusions

A one dimensional model of reactions, heat and mass transfer was set up to evaluate influences on self-heating and ignition of biomass. The central aim
of the model was to predict under which conditions biomass dust accumulations would spontaneously ignite. The reaction mechanism was developed in a previous study by thermogravimetric analysis (Chapter 4). Further modelling parameters, especially material properties of the solid biomass, gas phase properties, and heat and mass transfer correlations were taken from the literature. While measured CO and CO$_2$ data were used to assess the stoichiometric oxygen demand, it was found that the modelled off-gas distribution had little influence on modelling results.

The model compared favorably to lab-scale experiments on loosely packed beds of biomass dusts (see Chapter 5), especially considering that no relevant model parameters had been fitted to the fixed bed experiments. Ignition temperatures could be predicted within $-5\%$ error on the absolute temperature. A sensitivity analysis showed that the model was highly sensitive to the kinetic mechanism used. In contrast, modelling results were relatively insensitive to material properties (e.g., thermal conductivity, density) of the biomass. Unfortunately, from an application point of view, determining kinetic parameters for biomass oxidation is associated with rather high uncertainties. This is especially true for the low temperature range (ca. 325–475 K) of interest in self-heating and self-ignition problems. Material properties, on the other hand, are reported by several authors and are known with much better accuracy.

It was further found that the structure of the dust bed may play a role in self-heating, e.g. by influencing the effective thermal conductivity of the bed. Materials used in the lab scale study (Chapter 5) formed relatively homogeneous dust beds. The bulk solid was therefore treated in a simplified way in the model. However, this need not necessarily be the case for practical dust/particle accumulations as e.g. in power plant mills. It is suggested to investigate structural influences (e.g., particle size and density distributions) further.

Conclusions drawn from a scaling study are that critical temperatures for ignition are mainly influenced by reaction kinetics, (geometric) sample size, bulk density and bed porosity (in descending order). Evaluating the scaling study also makes it plausible that mill fires (see Chapter 2.2) may be caused by self-ignition of settled biomass dusts, although no accurate full-scale data were presently available to validate this.
### 6.5. Symbols and abbreviations

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<thead>
<tr>
<th>symbol</th>
<th>quantity</th>
<th>base units</th>
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<tr>
<td>$A$</td>
<td>area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$a$</td>
<td>thermal diffusivity</td>
<td>m$^2$ s$^{-1}$</td>
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<tr>
<td>$C$</td>
<td>molar concentration</td>
<td>mol m$^{-3}$</td>
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<tr>
<td>$c_p$</td>
<td>specific heat capacity</td>
<td>J kg$^{-1}$K$^{-1}$</td>
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<td>$D$</td>
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<td>$E_a$</td>
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<td>Gr</td>
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<tr>
<td>$H$</td>
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<tr>
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<td>$h$</td>
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<td>$k_0$</td>
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<tr>
<td>$\kappa$</td>
<td>permeability coefficient</td>
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<td>Unit</td>
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<td>( \lambda )</td>
<td>thermal conductivity</td>
<td>( \text{W m}^{-1}\text{K}^{-1} )</td>
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<tr>
<td>( \nu )</td>
<td>apparent reaction order</td>
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<td>( \rho )</td>
<td>density</td>
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<tr>
<td>( \sigma )</td>
<td>Stefan-Boltzmann constant</td>
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<tr>
<td>( \phi )</td>
<td>porosity</td>
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\( A \) ash
\( C \) carbon
\( c \) contact
\( \text{crit} \) critical
\( \text{eff} \) effective
\( \text{evap} \) evaporation
\( \text{exp} \) experimental
\( \text{ext} \) external
\( f \) final
\( g \) gas
\( \text{gas} \) sum of permanent gases CO, CO\(_2\), H\(_2\)O
\( H \) hydrogen
\( i \) index for species
\( \text{ign} \) ignition
\( j \) index for species, \( j \neq i \)
\( \text{LHV} \) lower heating value
\( m \) mass
\( O \) oxygen
\( \text{ox} \) oxidation
\( \text{pyr} \) pyrolysis
\( R \) reaction
\( r \) index for reaction
\( \text{ref} \) reference
\( s \) solid
\( \text{sim} \) simulated
\( \text{STP} \) standard temperature and pressure
\( T \) temperature
\( \text{tot} \) total
\( \text{vol} \) volatiles
\( W \) water
\( w \) wall
\( \alpha \) convection
\( \varepsilon \) radiation
\( \lambda \) conduction

superscripts
- \( \dot{\square} \) per unit time (rate of \( \square \))
- \( \square' \) per unit area
- \( \square'' \) per unit volume
7. Conclusions and Outlook

Ignition of biomass in environments similar to those of power plant mills was studied in this work by means of lab scale experiments and modelling. Power plant operators reported from experience that fires may start in pulverizers used for wood pellets, unless operating temperatures are lowered to ≤420 K. Based on the available literature, it was hypothesized that fires in mills are caused by supercritical self heating of fuels which settle in mills and remain there for prolonged periods of time, at elevated temperatures and with access to oxygen.

7.1. Main findings

Single pellet study

▷ Self-ignition is caused by heterogeneous oxidation.

Self-ignition experiments were carried out with single pellets (0.25 g) in an externally heated reactor. Spontaneous ignition of beech and pine wood pellets in air occurred at ambient temperatures around 500 K and upward. Ignition was characterized by a sudden, sharp increase in temperature of the pellet, and a complete conversion of the organic fraction. During burnout, the pellet could reach temperatures up to 900 K and emitted a visible glow. This behavior was distinct from flaming ignition, which required higher ambient temperatures (>700 K). Despite exceeding this critical threshold on burnout, no transition between the glowing and flaming modes was observed in single pellet experiments. It was concluded that heterogeneous oxidation is the main mechanism leading to ignition and burnout of biomass samples at low temperatures.

▷ Oxidation and pyrolysis occur in parallel and at similar rates around self-ignition.

From measured emissions of CO and CO$_2$, it could be seen by way of a carbon balance that the oxidation is accompanied by a pyrolysis of similar magnitude or rates. This agreed with the large amount of visible fumes emitted from the pellet. While these were not analyzed further, it could be inferred from works by other researchers that these volatiles contain the ‘missing’ carbon
For self-ignition, biomass is more than the sum of its components.

Additional experiments were carried out with commercially acquired cellulose, lignin and xylan (as a hemicellulose model substance). It was found that these isolated components behaved differently from whole biomasses. Self-ignition of biomass can therefore not be explained as the sum of the behavior of its components. Nevertheless, it was investigated further how and to what degree the behavior of biomass could be linked to its composition.

Reaction kinetic study

Pyrolysis and oxidation rates at low temperatures can be distinguished by thermogravimetric analysis.

Kinetic parameters for oxidation and pyrolysis of biomass were determined in the temperature range of 423–523 K, using stepwise isothermal thermogravimetric experiments. Six biomasses were investigated: two raw woods (beech, pine), two agricultural residues (sunflower husk pellets, wheat straw) and two types of commercial wood pellets. Oxygen concentrations were 0%, 20% and 80%. A model of four parallel reactions was fit to the pyrolysis data. Components that are tracked are the volatilizable amounts of extractives, hemicellulose, lignin and cellulose. The composition of the biomasses was analyzed to find the relative amounts of each component. The non-volatilizable (char) fraction of each component was estimated from thermogravimetric data of pure cellulose, lignin and xylan. Reactions of the biomass components could be modelled with the same activation energy, regardless of which biomass the components appeared in.

A single n-order reaction for oxidation of volatilizable components, plus a four-component pyrolysis model, describes the experimental data with good accuracy.

Two models for oxidation reactions were considered, one in which the volatilizable fractions of extractives, hemicellulose, lignin and cellulose react at a uniform rate, and one where individual kinetic parameters were assigned to each component. Char oxidation was always modelled separately. Char oxidation was expected to have little influence in the temperature range of interest, and included only for consistency with works found in the literature. Agreement between both oxidation models and data from the stepwise isothermal experiments was good. Pyrolysis and oxidation mechanisms also compared favorably to TGA-data measured at 5 K min$^{-1}$ between 373–773 K in 0%, 10% and 20% oxygen. The pyrolysis models were able to represent the entire range of the constant heating rate experiments, while the oxida-
CHAPTER 7

tion models could be extrapolated to temperatures up to 550–650 K. For the lumped volatilizable species, oxidation reactions had an apparent activation energy of 130 kJ mol\(^{-1}\), and an apparent reaction order in oxygen of 0.4–0.5. ▷ Reaction behavior is influenced by the composition of the biomass.

Biomass rich in potassium (e.g., wheat straw, sunflower husk pellets) appeared to pyrolyze and oxidize faster at elevated temperatures (>500 K), as could be anticipated based on available literature. At low temperatures (<470 K), biomass with high amounts of extractives (sunflower, pine) showed the highest mass loss rates. There appears to be change in the dominating mechanism: Low temperature (<470 K) reactivity was controlled by extractives; that at higher temperatures by hemicellulose and at even higher temperatures, by cellulose.

Lab-scale fixed bed study

▷ Oxidation reactions are detectable from 360 K upward.

Self-heating and self-ignition of loosely packed biomass dust beds were investigated in controlled heating experiments. Samples of 10–40 g were placed in a cylindrical wire mesh basket and gradually heated (1 K min\(^{-1}\)) to set final temperatures. Oxygen atmospheres were set to 0 %, 8 % and 20 %. Onset of oxidation reactions was detected by CO and CO\(_2\) emissions from temperatures as low as 360 K. CO and CO\(_2\)-rates were always higher when oxygen was present, regardless of temperature. For increasing temperatures and with oxygen present, the sample could either stabilize or ignite, with a critical ambient temperature to separate these two cases. Stable reactions were in this case characterized by a mild temperature overshoot (<20 K) and continuous emission of low amounts of CO and CO\(_2\). Ignition resulted in sudden increase of sample temperatures by several 100 K, an increase of CO and CO\(_2\) emissions, measurable depletion of oxygen, and a near complete burnout of the sample. Samples were found to heat inside out, i.e. the highest temperatures were measured in the sample center.

▷ Large sample masses, higher oxygen concentrations promote ignition. Particle size may have a minor effect as well.

The effect of sample size/bulk density, oxygen concentration and particle size were investigated for pine wood. Increasing the sample mass (at constant sample volume) could lead to ignition: more tightly compressed samples would ignite at temperatures for which more loosely packed (and thus lighter) beds remained stable. Samples in 20 % had lower critical temperatures required for ignition compared to samples in 8 % oxygen atmosphere. Oxygen availability did not significantly affect the onset temperature of CO
and CO$_2$, however. Particle size could affect the shape or structure of the dust bed (e.g., its porosity). While oxygen diffusion limitations were estimated to be negligible based on estimate calculations, the bed structure may affect the bulk thermal conductivity, and thus heat dissipation in the bed.

▷ Self-heating and ignition appear to be kinetically controlled.

Comparing four different biomasses (beech, pine, sunflower and wheat as used in the kinetic study), showed that these biomasses behaved similar in the fixed bed experiments as they did in thermogravimetric analysis.

**Modelling of self-heating and thermal runaway**

▷ A one-dimensional model for reactions, heat and mass transfer can predict ignition of the lab scale experiments with good accuracy. Agreement between model and experiment can be achieved without fitting parameters.

A one-dimensional, time- and space discrete model of reactions, heat and mass transfer was developed, with the aim of predicting critical conditions leading to self-ignition. Several of the lab-scale experiments were simulated for model validation. The model predicted ignition temperatures within $-5\%$ error, i.e., predicted ignition temperatures were always slightly lowered than the corresponding measured values. The kinetic parameters derived from thermogravimetric analysis were used in the reaction mechanism. Material properties used were mainly taken from the literature. Thus, the model did not involve fitting any parameters to fixed bed experimental data.

▷ Ignition predictions are highly sensitive to the kinetic model.

A sensitivity analysis was carried out to evaluate the relative importance of the different parameters used in the model. The model was most sensitive to reaction rates and the heat of reaction, i.e., in combination, the heat release kinetics. Parameters governing internal heat transfer had (only) a minor influence. Typically, uncertainty in estimating material properties is lower than that associated with reaction rates. Values for material properties of various biomasses are moreover available in the literature. For the cases tested, self-heating and ignition did not appear to be limited by mass transfer (oxygen diffusion).

▷ Large sample sizes, large bulk densities and high oxygen concentrations are risk factors for ignition.

Influences of sample size and operating conditions were investigated with the validated model. Critical temperatures for ignition showed a logarithmic trend with sample size, sample mass and oxygen concentration. Increasing the characteristic dimension of the sample by a factor of 2 could lower crit-
ical ambient temperatures by 15–20 K. Doubling bulk density lowered the critical temperature by approximately 10 K (at constant bed porosity) or 5 K (at constant solid density). Ignition temperature predictions increased only mildly when ambient oxygen was reduced. Sensitivity to oxygen is likely slightly underestimated in the present model.

**Summary**

In answer to the questions posed at the outset of this work (Chapter 2), the following can be concluded:

It appears highly plausible that mill fires are caused by low temperature oxidation. The process gradually builds up heat and can eventually lead to self-ignition, if ambient temperatures are sufficiently high.

A reaction kinetic model was developed, and values for the kinetic parameters were determined by thermogravimetric analysis at temperatures relevant to self-ignition and self-heating in mills. It was however also observed that this method can likely not be indefinitely extended to lower temperatures. Signal to noise ratio decreases for very low temperatures in the equipment which is presently state of the art. Measuring kinetic parameters at too high temperatures may miss reactions with low activation energy, that would be important at lower temperatures.

Despite these possible shortcomings, the reaction mechanism developed in this work compared quite favorably to experimental data - both on a very small scale (thermogravimetry), as well as when incorporated into a larger model, also including heat and mass transfer. The model for self-heating and ignition in dust beds was highly sensitive to the kinetic model. This underlines once more that the key to understanding and predicting self-ignition is in modelling exothermal reactions with sufficient accuracy, ideally over a broader temperature range.

Tendency to ignite could to some degree be traced to the composition of the biomass. High amounts of extractives typically led to an early/low temperature reaction onset. This did however not appear to be decisive for the temperature range in which ignition and thermal runaway were observed in this work (470–510 K). Rather, the biomasses with the highest reaction rates in the aforementioned temperature range (and also the lowest ignition temperatures) where those rich in inorganic elements, especially potassium. For the time being, both high content of extractives as well as catalytically active inorganics should be considered risk factors for self-ignition.
7.2. Suggestions for further work

Owing to the limited set of biomasses investigated in this study, no statistical analysis of the effect of composition on self-ignition temperatures could be made. It is suggested to broaden research in this area, and to report compositional data as well as inorganic elements together with kinetic parameters for biomass. Tentatively, it can be hypothesized that catalytic effects of potassium on cellulose (which are well described in the literature) also have an important role in transition from stable self-heating to spontaneous ignition. More data could help in confirming or rejecting this assumption. From an application point of view, it would be interesting if the fuel analysis data could already give an initial crude, but reliable, assessment of a material’s susceptibility to spontaneous ignition.

Secondly, it was noted that there is a shortage of reliable kinetic data for biomass reactions at low temperatures. In this work, it was noted that classical thermogravimetric analysis comes to a limit when temperatures are very low. Mass loss rates decrease, and it becomes difficult to evaluate the data. As outlined in Chapter 2, some advances have been made with calorimetric methods, especially when combined with measurements of gas concentrations. It would be interesting to combine several of the available experimental methods, to see whether this can improve the understanding of low temperature reactions.

Finally, the model developed in this work should be validated for full scale data. Such data were unfortunately not available for this work. On lab scale, parameters of the bed, e.g. particle size distribution, could only be varied in a very narrow range. Full scale measurements could reveal whether there are additional parameters of interest, that are missed on lab scale.
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A. Appendix

A.1. Oxidation of cellulose and xylan pellets

Figure A.1 shows the decomposition of a xylan pellet at oven temperature 513 K. The results were qualitatively similar to those for 573 K oven temperature. Heating occurred slower, so that the initial ‘melting’ phase was captured with a better image quality. The char retrieved at the end of the experiment was solid, dry, and highly porous.

Figure A.2 shows the decomposition of the cellulose pellet at 573 K oven temperature, compare Figs. 3.8, 3.9 and 3.10. Glowing of the pellet is faint and not visible against the external lighting.

Figure A.1.: Decomposition of a xylan pellet at 513 K
A.2. Kinetic parameters

A.2.1. Reproduction of published experiments

Some published experiments were reproduced to ensure the validity of the thermogravimetric measurements. Grønli et al. [157] published a round-robin study on pyrolysis of cellulose. The experiment at 5 K min\(^{-1}\) was reproduced and compared to the model published in [157]. The measured peak decomposition rate temperature in this experiment was on the higher end (605 K) of the range reported in the original study (600 K ± 5 K), Figure A.3. Instead of Avicel cellulose, cellulose from Sigma-Aldrich was used. Total gas flow rate was 150 mL min\(^{-1}\) of nitrogen.

Two experiments for pyrolysis of pine published by Grønli et al. [98] and Anca-Couce et al. [134] were also reproduced. Results are summarized in Figure A.4. Of the models presented by Grønli et al. [98], the biomass named "pine A" showed a better agreement with the measured data in this work. The model consists of four components, extractives, hemicellulose, cellulose and lignin [98]. Anca-Couce et al. [134] consider only hemicellulose, cellulose and lignin as components. The experimental in this work was measured at a constant heating rate of 5 K min\(^{-1}\) and a nitrogen flow rate of 150 mL min\(^{-1}\). The measured data shows slightly higher conversion rates than either model below 523 K. Between 550–650 K, experimental data of this work falls between the two models [98, 134].

A comparison between the kinetic models [98, 134] and experiments carried out at 423–523 K is shown in Figure A.5. The experiment consisted of
Figure A.3.: Reproduction of a round-robin study on cellulose pyrolysis kinetics. Model data: [157], experimental data: cellulose, 5 K min$^{-1}$ heating rate, 150 mL min$^{-1}$ nitrogen.

Figure A.4.: Reproduction of published TGA experiments on pine pyrolysis kinetics. Model data from [98] refers to species “pine A”, model data from [134] is the model with three components hemicellulose, cellulose and lignin. Experimental data: pine, 5 K min$^{-1}$ heating rate, 150 mL min$^{-1}$ nitrogen.
Figure A.5.: Extrapolation of published pine pyrolysis kinetics. Model data from [98] refers to species "pine A", model data from [134] is the model with three components hemicellulose, cellulose, lignin. Experimental data: pine, 150 mL min$^{-1}$ nitrogen, six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each.

six isothermal holding stages (423 K, 443 K, 463 K, 483 K, 503 K and 523 K) held for one hour each, with rapid heating of 10 K min$^{-1}$ between stages and to reach the first isothermal stage. Gas flow rates were 150 mL min$^{-1}$ of nitrogen. Experiments reported by Grønli et al. [98] were originally carried out at 383–773 K, 5 K min$^{-1}$ heating rate and 150 mL min$^{-1}$ nitrogen flow. Anca-Couce et al. [134] report data for 473–723 K and heating rates 2.5–10 K min$^{-1}$, so that the models presented in [98,134] are strictly only valid under those conditions. The comparison shows that the models do not extrapolate very well to low temperatures and low heating rates or isothermal conditions. The model of Grønli et al. [98] predicts mass loss well during the first three isothermal stages 423–463 K, but overpredicts mass loss for higher temperatures. The model by Anca-Couce et al. [134] predicts lower mass loss rates than measured between 423–463 K, and higher rates than measured for 483–523 K.

### A.2.2. Kinetic control

Experiments under transient heating conditions can become limited by heat transfer, if heat transfer to and within the particle are not significantly faster than reaction rates [159]. Heat transfer limitations in the pyrolysis experi-
ments were checked against criteria presented by Hayhurst [160]. Following that work, experiments with transient heating need to satisfy:

$$\text{Bi} = 0.6 \frac{\text{Nu}}{2} \frac{\lambda_g}{\lambda_s} < 0.1$$  \hspace{1cm} (A.1)

where Bi is the Biot number, Nu the Nusselt number and \( \lambda_g \) and \( \lambda_s \) the thermal conductivities of gas and solid, respectively. Approximating \( \text{Nu} = 2 \) for spherical particles in near stagnant flow [160], as well as biomass solid thermal conductivities \( \lambda_s = 0.12-0.18 \text{ W/(m K)} \) [19] and thermal conductivity of air or nitrogen \( 0.04 \text{ W/(m K)} \) at 523 K [19], Bi = 0.13–0.2. This value is slightly higher than that used in the literature [160], yet still smaller than unity (equal timescales of external and internal heat transfer). As discussed in [160], the above expression does not depend on particle size, if gas velocities are low enough that size influences on Nu are negligible.

The Biot number was also estimated for the entire sample, i.e. the crucible with the particle bed. The crucible is approximated as a spherical object in near-stagnant flow, so that \( \text{Nu} = 2 \). Thermal conductivity of the crucible material (alumina) is one order of magnitude higher than that of wood (\( \lambda \approx 2 \text{ W m}^{-1} \text{K}^{-1} \)), so that it does not limit heat transfer through the bed. Thermal conductivity of the particle bed depends on the thermal conductivities of solid particles and interstitial gas, as well as the porosity \( \phi \) of the bed. Assuming loosely packed beds, \( \phi = 0.5-0.8 \), and an effective thermal conductivity [16] of

$$\lambda_{\text{eff}} = \phi \lambda_g + (1 - \phi) \lambda_s$$  \hspace{1cm} (A.2)

Biot-numbers for the sample evaluate to 0.2–0.4. Temperature in the sample bed is therefore mainly, but not exclusively controlled by external heat transfer. Approximate kinetic control was nevertheless assumed, as Bi < 0.1 is difficult to achieve in practice [160].

As internal heat transfer is faster than external heat transfer, the external Pyrolysis number Py, i.e. the rate of external heat transfer to reaction rate [159], was evaluated. To assume kinetic control, in addition to Bi \( \ll 1 \), the timescale of reactions must be much larger than that of heat transfer, \( \text{Py} = \tau_{\text{kin}}/\tau_{\text{heat}} \gg 1 \), where \( \tau_{\text{kin}} \) is the kinetic timescale and \( \tau_{\text{heat}} \) the heat transfer timescale. The criterion gives a maximum value for the particle radius \( r \) [160]:

$$\frac{2 \rho c_p r^2}{3 \text{Nu} \lambda_g} < 0.1 \cdot \tau_{\text{kin}}$$  \hspace{1cm} (A.3)

where \( \rho \) is the density of the solid and \( c_p \) its specific heat capacity. The
kinetic timescale is estimated as $\tau_{\text{kin}} = 1/k$, where $k$ are the modelled reaction rates. Reaction rates are below $1 \times 10^{-3}$ s$^{-1}$ for temperatures below 523 K. Assuming $\rho = 600$ kg m$^{-3}$, [19] and $c_p = 2000$ J/(kg K) [16], this allows for particle sizes up to 6 mm diameter. The above expression was also used to calculate the critical rate for 250 µm particles (the largest particle size used) results in $k = 0.6$ s$^{-1}$. Such rates were only predicted above 700 K for pyrolysis and above 625 K for the oxidation models. The same calculation was carried out for the entire bed of particles, i.e. for lower densities (bulk density instead of solid density). Again assuming $\text{Nu} = 2$ and using the bed depth (1/3 of 4 mm) instead of the particle radius, critical reaction rates would be reached at temperatures of 555 K (20% oxygen, $\phi = 0.5$), 570 K (20% oxygen, $\phi = 0.8$), 590 K (pyrolysis, $\phi = 0.5$) and 620 K (pyrolysis, $\phi = 0.8$). Critical temperatures are lower for the oxidation experiments as total reaction rates are higher when oxygen is present.

In the oxidation experiments, lack of oxygen can inhibit kinetic control in addition to possible heat transfer limitations. For the loosely packed sample in the crucible, diffusion through the bed is the main mode of mass transfer. The ratio of oxygen consumption to oxygen diffusion can be expressed by a Damköhler number $Da$. In this work, it was estimated by:

$$Da = \frac{k(T) \cdot f(p_{O_2}) C_{O_2,\text{stoich}} L^2}{D C_{O_2,\text{amb}} L^2}$$  \hspace{1cm} (A.4)

where $k(T) \cdot f(p_{O_2})$ is the reaction rate including oxygen partial-pressure dependency, $C_{O_2,\text{stoich}}$ the concentration of oxygen required for complete conversion (i.e., molar amount of oxygen per unit volume occupied by the sample), $C_{O_2,\text{amb}}$ the concentration of oxygen in the surroundings and $D$ the diffusion coefficient. $L$ is a characteristic length, in this case, the sample depth, 1.3 mm (one third of the crucible height). Kinetic control is given for $Da \ll 1$. The kinetic expression was evaluated for wheat, using the rate of oxidation model I. The diffusion coefficient was estimated by

$$D = 1.5 \times 10^{-5} \left( \frac{T}{T_{\text{ref}}} \right)^{1.75} ; \quad T_{\text{ref}} = 300 \text{ K}$$  \hspace{1cm} (A.5)

Stoichiometric oxygen demand can be calculated from the elemental composition. Ambient oxygen concentrations were calculated assuming a pressure of 101325 Pa, 20% oxygen, and by assuming sample and surroundings in thermal equilibrium. Based on these values, diffusion is much faster than consumption of oxygen ($Da < 0.1$) for $T < 570$ K.

Thermal runaway of samples can occur when heat is (locally) released faster than it can be dissipated by internal heat transfer. Such possible self-ignition
of the sample was evaluating the dimensionless Frank-Kamenetskii parameter [48] \( \delta \):

\[
\delta = \frac{h_R \rho}{\lambda_{\text{eff}}} E_a \frac{L^2}{R T^2} \cdot k(T) \cdot f(p_{O_2}) \tag{A.6}
\]

where the mass-specific enthalpy of reaction \( h_R \) was set equal to the lower heating value of wheat (18.2 MJ/kg), the bulk density of the sample was \( \rho = 97 \text{ kg m}^{-3} \), the effective thermal conductivity of the sample \( \lambda_{\text{eff}} = 0.07 \text{ W m}^{-1} \text{K}^{-1} \). The sample depth was used as characteristic length \( L \). According to the theory of thermal explosions, samples are stable, i.e., do not self-ignite, when \( \delta < \delta_{\text{crit}} \). The critical values \( \delta_{\text{crit}} \) depend only on geometry, and are given as 0.88 for infinite slabs, 2.00 for infinite cylinders and 3.23 for spheres [48]. In the worst-case assumption, the sample was treated as an infinite layer. Evaluating \( \delta \) as a function of temperature \( T \) gave a critical temperature of 530 K. Assuming the sample can be represented by a sphere resulted in \( T_{\text{crit}} = 555 \text{ K} \). Repeating this calculation for 80% oxygen, i.e. higher reaction rates, gave critical temperatures of 520 K and 540 K, respectively. Heat release kinetics are likely overestimated in the above calculation, as the smoldering conversion typical of the temperature range investigated leads to highly incomplete conversion [123] (and thus lower heat release). Additionally, thermal runaway should be fairly easy to observe if it occurred at low heating rates or during the isothermal stages – however, no excessive (uncompensated) self-heating was measured in any of the experiments.

In conclusion, which transport limitation is most critical with respect to assuming kinetic control depends on the type of experiment. The largest concern in experiments with constant heating rate was the Biot-number. For the stepwise isothermal experiment, this can be neglected, as the transient phases are short compared to the isothermal holding periods. As discussed by Hayhurst [160], the Biot-number depends largely on material properties, and values \( 1 < \text{Bi} < 0.1 \) are difficult to avoid for biomass. Possible self-ignition of the sample could be a concern in experiments with oxygen present. By conservative estimate, samples may come close to thermal runaway during the TG-experiments. Thermal runaway was however not observed experimentally. Diffusion limitations were found to be negligible in the temperature range of interest. All estimations of critical parameters were carried out by neglecting the influence of conversion on reaction rates. Measured conversion rates were much lower (< 0.0015 s\(^{-1}\)) than the reaction rates (compare the Arrhenius plots) used in the above calculations, so that the critical parameters include a considerable safety margin. The stepwise isothermal experiments are expected to be free from transport limitations, even if the above strict criteria are applied.
A.2.3. Kinetic data for cellulose, lignin, xylan and rapeseed oil

Kinetic parameters for the model components extractives, hemicellulose, lignin and cellulose were determined by thermogravimetric analysis and using the same time-temperature programs as for the six biomass samples. Rapeseed oil was used as a model compound for extractives. To simulate extractives bound in a matrix (i.e. as opposed to a bulk liquid), the oil was mixed in a ratio of 1:1 by weight with SiO$_2$ as an inert substrate. The consistency of the mixture was that of a thin paste. Alternative mixtures of rapeseed oil and cellulose, and of linseed oil and either SiO$_2$ or cellulose were also investigated, but gave qualitatively similar results. As a model compound for hemicellulose, xylan (from cornstalk; abcr Chemie AB143294) was used. Lignin and cellulose were also acquired from a commercial supplier (alkali lignin: Sigma-Aldrich 471003, and cellulose powder: Sigma-Aldrich C6288).

Char yields of the model components were measured by heating in inert atmosphere at 5 K min$^{-1}$ to 773 K, holding that temperature for 30 minutes, followed by a burn-off under 10% oxygen and 10 K min$^{-1}$ heating rate to 973 K. Results of the heating in inert atmosphere are summarized in Figure A.6 for xylan, lignin and cellulose. Extractives were assumed to be completely volatilizable, either by pyrolytic decomposition or by evaporation. The residues at 773 K were approximately 9% for cellulose, 25% for xylan

![Figure A.6.: Experiments at 5 K min$^{-1}$ heating rate under 0 % oxygen to determine the volatilizable fractions of hemicellulose, cellulose and lignin. Xylan was used as a hemicellulose model component.](image-url)
APPENDIX A.2

and 65% for lignin. On burnout, cellulose and xylan left no residue, while the lignin sample left around 5% ash residue. Char ratios of the three components were therefore 9:25:60 (cellulose:xylan:lignin), which was rounded to 10:30:60 in the model.

Activation energies of extractives, hemicellulose, lignin and cellulose were determined by the same stepwise isothermal heating program used for the six biomasses: holding for one hour each at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K, with rapid heating (10 K min$^{-1}$) to reach the first isothermal period and in between isothermal stages. Experiments were carried out under 0%, 20% and 80% oxygen. Kinetic parameters were then obtained by the same model as for the six biomasses, i.e. total conversion rate is the sum of pyrolysis and oxidation rate

$$\frac{dX_i}{dt} = k_{\text{pyr}, i} \cdot (1 - X_i(t))^{n_{\text{pyr}, i}} + k_{\text{ox}, i} \cdot (1 - X_i(t))^{n_{\text{ox}, i}} \cdot \left(\frac{P_{O_2}}{P_{\text{ref}}}\right)^{n_{O_2, i}} \quad (A.7)$$

for each component $i$. Reactions were assumed to be $n$-order and reaction rates $k$ were modelled by an Arrhenius-expression as outlined above. Kinetic parameters were found by a least-square fit of the reaction model to the measured data. This was carried out in two steps: the parameters of the pyrolysis reaction $\{E_a, k_0, n_{\text{pyr}}\}$ were determined first from experimental data under 0% oxygen. These parameters were then kept fixed, while those of the oxidation reaction $\{E_a, k_0, n_{\text{ox}}, n_{O_2}\}$ were fitted. The numeric results are summarized in Table A.1, and modelled and experimental data are compared in Figures A.7 through A.10. The value of the kinetic parameters depended to some degree on the final mass $m_{f, i}$ that was assumed in their fitting. For xylan, lignin and cellulose, the remaining mass fraction for pyrol-

<table>
<thead>
<tr>
<th>$m_f/m_0$ [kg/kg]</th>
<th>Rapeseed oil+SiO$_2$</th>
<th>Xylan</th>
<th>Lignin</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>0.5</td>
<td>0.25</td>
<td>0.65</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table A.1.: Kinetic parameters for volatilizable fractions of extractives, hemicellulose, lignin and cellulose. Rapeseed oil mixed (50% by weight) with SiO$_2$ as inert substrate was used as a model compound for extractives in a matrix. Xylan was used as a model compound for hemicellulose.
ysis up to 500 °C (Figure A.6) was used. For the rapeseed-oil-SiO$_2$ mixture, it was assumed that all oil is reacted or evaporated and only the inert substrate remains.

Over the temperature range 423–523 K, xylan showed the highest mass loss. However, lignin and the rapeseed-oil-SiO$_2$ mixture have high 'baselines' of inert material (65% and 50%, respectively), so that the relative loss of reactive material is also considerable in the temperature range investigated. Cellulose showed very little mass loss during the lower temperature stages of the experiment, but reactions were found to rapidly accelerate beyond 503 K.

The overall behavior of lignin interestingly resembled that of native biomasses from a qualitative point of view. Similar to the native biomasses, its behavior is only approximated by the combination of two n-order reactions for pyrolysis and oxidation. Rapeseed oil, xylan and cellulose on the other hand showed very specific trends. The decomposition of xylan did not appear to be affected by the concentration or presence of oxygen. The modelled oxidation reaction has very low rates, so that the three model curves for 0%, 20% and 80% oxygen collapse onto the pyrolysis curve. Two explanations are possible: either oxidation of xylan is very slow compared to its pyrolysis, or the experiment was not kinetically controlled. Several researchers working in temperature ranges from ambient temperature to 800 K or higher

![Figure A.7: Modelled and measured mass loss of rapeseed oil on SiO$_2$ powder, mixed 1:1 by weight. Six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each, different oxygen concentrations.](image)
Figure A.8.: Modelled and measured mass loss of xylan. Six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each, different oxygen concentrations.

Figure A.9.: Modelled and measured mass loss of lignin. Six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each, different oxygen concentrations.
consider 5 mg sufficiently small to avoid diffusion limitations [98, 136, 138, 140, 143, 146, 161], while some allow up to 10 mg [133, 137, 139, 144]. Sample masses were 6.8 mg, 6.5 mg and 7.1 mg in the experiments show in Figure A.8, while final temperatures and heating rates were lower in our experiments (implying lower reaction rates) than those reported in the literature [98, 133, 136–140, 143, 144, 146, 161].

It was also noted that the xylan powder was very hygroscopic and would immediately absorb humidity from the surrounding air when preparing the samples, forming sticky agglomerates in the process. This may have led to additional transport limitations. Ultimately, the reasons for the observed behavior of xylan could not be resolved. The activation energy reported for xylan in Table A.1 was initially used to model the hemicellulose component of the biomass, but replaced with higher values for reasons described in the results section of this work.

Pyrolysis reactions of both the rapeseed oil mixture and cellulose could be equally well represented by a first or zero-order reaction in the temperature range 423–523 K. The reaction order did not appear to affect the respective values determined for the activation energies.

Comparing the kinetic parameters for the pure components in Table A.1 with those for the components as they appear in the biomasses (see main text) shows rather large differences in the pre-exponential factors \( k_0 \) and reaction orders \( n \). This behavior is expected, owing to physical and chemical
changes introduced during separation procedures, neglecting interactions among components and absence of catalytic effects of inorganic matter when studying the isolated components [100].

A.2.4. Comparison of oxidation models I and II

Oxidation models I and II showed only minor differences in the temperature region of interest, 423-523 K. A comparison of model I and measured data can be seen in the main body of the text. The corresponding plots for model II are found in Figure A.11. Differences between the models become apparent at temperatures above ca. 520-550 K for a heating rate of 5 K min$^{-1}$.

Table A.2 lists the scaled root-mean-square deviations of both oxidation models compared to measured data. Both models represent measured data with similar accuracy.
Figure A.11.: Oxidation model II: comparison of isothermal experiment and model, assuming separate oxidation kinetics of hemicellulose, cellulose, lignin and extractives. Kinetic parameters are listed in the main text.
Table A.2.: Scaled root-mean-square deviations ($\delta_{S,\varphi}$) between modelled and measured data in oxidative atmosphere. “Isothermal” refers to the stepwise isothermal experiments, “ramp” to those at constant heating rate 5 K min$^{-1}$.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Model</th>
<th>$\delta_{S}(m/m_0)$</th>
<th>$\delta_{S}(dX/dt)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20 % O$_2$ ([$%$])</td>
<td>80 % O$_2$ ([$%$])</td>
</tr>
<tr>
<td>Isothermal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beech</td>
<td>I</td>
<td>1.25</td>
<td>1.53</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.84</td>
<td>0.91</td>
</tr>
<tr>
<td>Pine</td>
<td>I</td>
<td>5.55</td>
<td>4.27</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.72</td>
<td>1.25</td>
</tr>
<tr>
<td>Sunflower</td>
<td>I</td>
<td>1.15</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.73</td>
<td>0.81</td>
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<td>Wheat</td>
<td>I</td>
<td>3.79</td>
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</tr>
<tr>
<td></td>
<td>II</td>
<td>1.87</td>
<td>1.29</td>
</tr>
<tr>
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<td>2.40</td>
<td>2.15</td>
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<tr>
<td></td>
<td>II</td>
<td>0.88</td>
<td>1.32</td>
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<tr>
<td>Wood pellets I2</td>
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<td>2.79</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>2.46</td>
<td>1.53</td>
</tr>
<tr>
<td>5 K min$^{-1}$ ramp</td>
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<td>20 % O$_2$ ([$%$])</td>
<td>10 % O$_2$ ([$%$])</td>
</tr>
<tr>
<td>Beech</td>
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<td>2.65</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.73</td>
<td>1.46</td>
</tr>
<tr>
<td>Pine</td>
<td>I</td>
<td>5.09</td>
<td>5.53</td>
</tr>
<tr>
<td></td>
<td>II</td>
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<td>3.26</td>
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<td>3.43</td>
<td>3.84</td>
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<tr>
<td></td>
<td>II</td>
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</tr>
<tr>
<td></td>
<td>II</td>
<td>4.89</td>
<td>4.72</td>
</tr>
</tbody>
</table>
A.2.5. Use of K-content to determine cellulose pyrolysis kinetics

Inorganic elements are well-known to catalyze the pyrolysis of biomass [100, 101, 155]. Catalytic effects of potassium have been reported for cellulose [86, 150, 155, 163, 164] and hemicellulose components [150, 163]. Our experiments were consistent with the literature, in that the temperature of peak pyrolytic decomposition rate scaled with the potassium content of the samples, Figure A.12. The peak in pyrolysis decomposition rate is typically associated with the cellulose component [100]. A linear correlation can be found for the pre-exponential factor for cellulose pyrolysis $k_{0,\text{pyr,CELL}}$ to reproduce these temperatures ($E_{a,\text{pyr,CELL}} = 185 \text{kJ mol}^{-1}$) as a function of the cellulose mass fraction $w_K$ [kg kg$^{-1}$]:

$$k_{0,\text{pyr,CELL}} = (9.34 \times 10^{15} \cdot w_K + 2.37 \times 10^{12} \pm 2.29 \times 10^{12}) \cdot \text{s}^{-1} \quad (A.8)$$

The correlation and the actual values used in the pyrolysis model are seen on the right side of Figure A.12. Comparing the model predictions for the cellulose components with measured data for pure cellulose (Figure A.13), it can be seen that the models predict a broader range of decomposition than that seen for isolated cellulose. The peaks for sunflower and wheat cellulose components appear at lower temperatures than that of pure cellulose, those of pine and the two wood pellet samples are delayed.

Figure A.12.: Peak pyrolysis rates and potassium content: The temperature of peak conversion rates $T_{\text{peak}}$ correlates with biomass potassium content (left). This correlation can be used to estimate the interval of $k_{0,\text{pyr,CELL}}$ (right, dashed lines), for an apparent activation energy of 185 kJ mol$^{-1}$. Points represent the values used in the pyrolysis models of the six biomasses.
A.2.6. Modelled conversion of biomass components

Figures A.14 through A.19 show the cumulated conversion of extractives, hemicellulose, lignin, cellulose and char as predicted by the pyrolysis model (left), oxidation model I at 20% oxygen (center) and oxidation model II at 20% oxygen (right), as predicted for the stepwise isothermal experiments 423–523 K (compare main text) The figures illustrate how the different components of the biomasses are gradually consumed in the isothermal experiments, starting with the most reactive fractions (extractives and hemicellulose). No consumption of char is predicted. Conversion of cellulose is weak for the pyrolysis cases, and only occurs in the final isothermal stages. The main difference between oxidation model I and II is in the relative conversion of cellulose and hemicellulose. Model II predicts very little cellulose conversion (in agreement with the pure cellulose experiments the model is based on). Lignin conversion does not differ much between the two oxidation models, as the global oxidation kinetic parameters (model I) and those of the lignin component (model II) are very similar.
Figure A.14.: Beech: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled fractions are ash (bottom) and extractives (top). Labels (I) and (II) refer to oxidation models I and II, respectively.

Figure A.15.: Pine: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled top fraction is extractives, ash content is < 0.01. Labels (I) and (II) refer to oxidation models I and II, respectively.

Figure A.16.: Sunflower: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled fractions are ash (bottom) and extractives (top). Labels (I) and (II) refer to oxidation models I and II, respectively.
Figure A.17.: Wheat: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled fractions are ash (bottom) and extractives (top). Labels (I) and (II) refer to oxidation models I and II, respectively.

Figure A.18.: Wood pellets I1: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled top fraction is extractives, ash content is < 0.01. Labels (I) and (II) refer to oxidation models I and II, respectively.

Figure A.19.: Wood pellets I2: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled top fraction is extractives, ash content is < 0.01. Labels (I) and (II) refer to oxidation models I and II, respectively.
APPENDIX A.3

A.3. Fixed bed experiments

A.3.1. Mechanical setup

The main part of the oven is a horizontal alumina tube with length 955 mm and internal diameter 51 mm, closed at both ends. The tube is heated from the outside by three independently controlled heating elements. The sample is placed in the middle segment, with the outer two segments acting as an ‘active’ insulation to maintain a constant temperature in the tube. Each heated segment is controlled by a temperature controller model 2116 manufactured by Eurotherm Controls. The typical operation mode was to set a heating rate ramp, a final setpoint oven temperature, and a holding time.

The tube is supported on both ends by water-cooled, sealed flanges. Gas enters into the oven at one end and is removed at the opposing flange (compare Fig. 5.1). This creates a plug flow-type flow field within the oven. There is also a water cooled chamber of 170 mm usable length at the inlet end of the tube. The chamber can be used for either quenching the sample or storing it at low temperatures (e.g. while waiting for the oven to heat) without having to open the oven again to insert the sample.

The sample itself is placed in a cylindrical mesh wire basket, which is suspended from a stainless steel tube. An additional thin support ensures that the sample is placed on the central axis of the oven tube. While the experiment is running, the tube is clamped by a nut with a teflon fitting on the cooling-chamber-side flange. The tube is hollow and is used as a lead for a thermocouple array. The sample basket is shown in Fig. A.20, where the supporting beam would be attached on the right (not shown) by thread. The sample holder is closed to avoid spilling of dust material while handling the sample, and also makes the sample symmetric, i.e. there are no free dust surfaces. The sample holder is shaped like a long cylinder with a length-diameter-ratio of l/d = 5. Dimensions of the sample holder are limited by the length of the middle heating section of the oven and the available cross section area. The cylinder walls are made of fine wire mesh, whereas the end faces are thin stainless steel plates.

The gas atmosphere in the oven is adjusted by mixing streams of pure nitrogen and oxygen. The corresponding mass flow controllers are calibrated within 0–6 L min$^{-1}$ (N$_2$) and 0–2 L min$^{-1}$ (O$_2$), respectively. Both flow rates are given at standard conditions. A thin (6 mm) PFA-tube is used to transport the gas from a mixing panel to the oven.

On the outlet end, all of the exhaust gases are transported via a heated tube to a gas conditioning unit. This consists of a first filter, a cooler, and a second
filter, followed by a sample gas pump. A valve at the outlet allows some of the gas to be directed to a set of gas analyzers, while the rest is exhausted via central ventilation. During the experiments, significant amounts of tar may be released, that condense near the cooled flanges, in pipes or in the conditioning unit. The condensed tar forms small droplets, which either precipitate on the tubing walls or are caught as aerosol in the filters. For this reason, the ceramic fiber filters are regularly replaced, and less frequently, the interconnecting tubing as well. Condensed vapors of tar and water are discarded.

A.3.2. Instrumentation and data sampling

The main quantities measured are temperature and the concentration of CO, CO$_2$ and O$_2$ in the off-gases. Additionally, the oven is equipped with a pressure gauge and the flow rate of sample gas to the analyzers can be measured. These values are however used for operation only and not recorded.

Temperature is measured using type K thermocouples with 1.5 mm diameter. Large diameter thermocouples are used because they can easily be bent into place. Temperature fluctuations are thought to be small enough, so that
no significant inertia effects are expected. One thermocouple measures the
temperature in the oven at a distance of several centimeters from the sample.
This is taken as the oven wall temperature, since the thermocouple is in
loose contact with the wall. Readings on the oven temperature controllers
are used for controlling purposes only, and are not recorded. Even at low
heating rates there is a significant time-lag between the controller readings
and the recorded oven temperature, owing to the thickness of the alumina
tube.

The thermocouples in the sample holder (see Fig. A.20) record the temper-
ature in the middle of the sample (r = 0), at the boundary (here: r = 15 mm)
and in the immediate vicinity of the sample (compare Fig. A.20c). These
values are referred to as center, boundary and envelope temperatures, re-
spectively. Lengthwise, they are positioned approximately in the middle of
the sample holder.

Gas is analyzed by an Emerson NGA 2000 analyzer with ranges as listed in
table A.3. Carbon monoxide and carbon dioxide are measured in the infrared
spectral range. Oxygen is measured with a paramagnetic sensor. Water and
other condensable liquids are removed in the gas conditioning unit. All re-
ported values are therefore dry measurements. Internally, the analyzer con-
sists of different measurement chambers for each channel. The gas passes
through these chambers in reverse order of the channels, i.e. oxygen is mea-
sured first and CO (low) last.

**A.3.3. Sample preparation and setup operation**

As a form of general maintenance, the gas analyzer is calibrated on a weekly
basis. The oven is visually inspected for residues of previous experiments.
If such leftovers are found, they are burned off by running the oven at very
high temperatures.

Materials are stored in sealed plastic jars prior to the experiment. They

<table>
<thead>
<tr>
<th>Channel</th>
<th>Gas</th>
<th>Range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO</td>
<td>0–4000</td>
<td>ppm</td>
</tr>
<tr>
<td>2</td>
<td>CO</td>
<td>0–30</td>
<td>Vol-%</td>
</tr>
<tr>
<td>3</td>
<td>CO₂</td>
<td>0–3000</td>
<td>ppm</td>
</tr>
<tr>
<td>4</td>
<td>CO₂</td>
<td>0–20</td>
<td>Vol-%</td>
</tr>
<tr>
<td>5</td>
<td>O₂</td>
<td>0–25</td>
<td>Vol-%</td>
</tr>
</tbody>
</table>

<sup>1</sup> calibrated with 5 Vol-% CO
are used as-is, i.e. no pre-drying is carried out unless otherwise mentioned. Samples are loaded into the holder, until the basket is completely filled (see Fig. A.20b). The sample is not compressed in any way. Therefore, it should adopt its natural bulk density and form a loosely packed bed. The weight of each sample is determined by measuring the difference between the sample jar before and after loading the basket. Possible spill is neglected.

The sample is then loaded into the oven – either directly into the heating zone (the majority of the experiments), or into the cooling chamber (for pulse ignition experiments). The nitrogen flow is set to the predetermined level, and the inlet gas line is connected. This immediately starts flushing the reactor with nitrogen. Readings on the gas analyzer are observed, until all measured gas concentrations (CO, CO$_2$ and O$_2$) are zero. This is used as a leakage test. Following this, oxygen is added to the desired gas concentration. The heating procedure is started only when gas flow rate and concentrations have reached the set values.

Heating of the oven elements follows a pre-described heating rate, which can be set between 0.1 K min$^{-1}$ and 10 K min$^{-1}$. The oven will then hold this temperature for a pre-defined time, and switch off afterwards. As the inner oven tube has to be heated thoroughly first, the temperature inside the oven follows that of the heating elements with considerable delay. For the same reason, the heating rate seen by the sample will not be constant throughout the experiment, but slower in the beginning and at the end of the heating process. Heating rate and hold time were varied in the initial series of the experiments. The majority of experiments was carried out at 1 K min$^{-1}$.

After each experiment, the sample is carefully removed from the oven and photographed. The mass of the reacted sample is again determined by the difference in weight of the filled and the empty, cleaned sample holder.

### A.3.4. Data acquisition and pre-processing

Data is sampled in 10 second intervals using LabVIEW-software distributed by National Instruments. Values from the gas analyzer are first transmitted to a central server recording data from all gas analysis units. The thermocouple measurements are read directly to the control computer, as is the control of the oxygen mass flow meter. Data from gas analyzer and the directly connected measuring units is synchronized and written to the same file. Data is stored in .xls files and converted to comma-separated-values for further processing.

Analysis of the data is done via a GNU Octave script. From a given recording, the part of the data is extracted between the time when the measured
Appendix A.3

Oven temperature first increases within 5 K of its initial value (start) and the time when the oven temperature falls 10 K lower than the maximum recorded value (end). The wall clock time is replaced by a timestamp since start of the experiment.

A synchronization of gas and temperature measurements is carried out to compensate for the long gas pathway from oven through gas conditioning, connecting tubing and the analyzer. The synchronization is based on the response of the oxygen signal to the opening of the oxygen valve. The necessary data is taken from the otherwise unused beginning of the recording. The time $t_1$ is defined as the point, at which the oxygen valve opens to 95% of its setpoint value. Following the valve opening, $t_2$ is the the time at which the measured oxygen concentration first reaches 5% of its overall maximum during the experiment. All gas concentration signals are then shifted by $\Delta t = t_2 - t_1$. The thus obtained dataset is referred to as synchronized data and used for further analysis. The original dataset is also retained separately. Figure A.21 illustrates this shift with data from an actual experiment. Here, nominal flow is the oxygen mass flow meter signal, the thin line corresponds to the original measured oxygen concentration, and the thick line is the synchronized signal. In the example, the time shift $\Delta t$ is approximately 2 minutes.

The reason for this treatment is that the thermocouple readings are instantaneous, whereas the gas sampling appears delayed due to the long gas path to the analyzers. The original measurements are therefore out of synchro-

![Figure A.21.: Example of a gas flow synchronization. Taken from an actual dataset and normalized – total flow rate 2.5 L/min at STP, 20% oxygen.](image-url)

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nization. The 5%-threshold on the oxygen signal was chosen as an estimate to automatically synchronize the events ‘valve opening’ and ‘first detection of oxygen’, but avoiding this to be influenced by fluctuations on the oxygen signal. A full modeling of the step-response of the system was tried, but abandoned due to the added complexity and the greater manipulation of the original data. The underlying assumptions in the method used is that the gas path from mass flow controller to the oven is (infinitely) short, and that the flow through the gas lines can be assumed as a plug flow. Using a low oxygen threshold avoids making any assumptions about the flow field in the oven, i.e. the residence time distribution is left intact. From a practical perspective, the method requires that experiments are started using a nitrogen-only flow.

A.3.5. Effect of synchronization

A coupling of sample temperature and emission of product gases CO and CO$_2$ is expected, since both are influenced by an exothermic oxidation reaction in the sample. However, the dynamic behaviors of the measurement devices, thermocouples and a multi-channel IR-gas analyzer, are different. Therefore, errors may arise when comparing temperature and gas concentrations to each other, especially when high gradients occur. The error can be minimized by deconvoluting the signals. This would however require more elaborate signal processing and knowledge of the transfer functions for temperature and gas species measurements. Instead, only a simple synchronization was carried out, which accounts for the delay but not for the spreading/smoothing of the gas analyzer signal. Temperature measurements were not processed further. The justification is that the thermocouples are expected to react (nearly) instantaneously, while the gas analyzer signal is delayed (due to the length of the tube between sample and analyzer) and its rate of change is damped (due to mixing, accumulation in the measurement chamber of the analyzer, etc.). This treatment however raises the question, whether additional sampling artifacts are introduced by the synchronization, e.g. by overcompensating the delay time.

In the following example, the region at which thermal runaway occurs is investigated both based on unsynchronized, raw data and on the synchronized, time-shifted data (Figs. A.22b and A.23) for one experiment (160908). In the example, the time shift by synchronization is approximately 2 minutes – about one half of the time the sample center temperature takes to rise from 523 K to 723 K. As is apparent from Fig. A.22b, the concentrations of CO and CO$_2$ increase, and O$_2$ decreases, at a much lower rate. It can also be seen in Fig. A.22a that the increase in CO and CO$_2$/decrease in O$_2$ occurs slightly before the pronounced temperature rise. This becomes more apparent when
Figure A.22.: Conditions at thermal runaway, experiment 160908. Indices $c$, $b$ and $e$ stand for center, boundary and envelope temperatures, respectively.

Figure A.23.: Effect of synchronization on temperature/species relation, experiment 160908
plotting gas concentrations over temperature, Fig. A.23a. The jump at 523 K shows where product gas concentrations increase faster than sample center temperature. The relatively flat regions of the curves, 573–723 K, are when the temperature has already increased and the gas concentrations follow slowly.

In the synchronized data, this effect is even more pronounced, and the jump is much sharper (Fig. A.23b). Comparing the synchronized time-series data, Fig. A.22b, shows that the synchronization now shifts the onset of CO and CO$_2$ increase to before the increase in temperature ($\approx$201 min vs. $\approx$204 min).

From this simple example, the following can be concluded:

1. The discontinuities seen in the gas concentrations-temperature curves are not caused by the signal synchronization, but they are amplified by it.

2. The data in itself does not allow to determine whether the effect is caused by the dynamic measurement behavior or whether it caused by the reaction of the sample.

3. The region of high gradients should be interpreted with great care.

### A.3.6. Experimental conditions

#### A.3.6.1. Comparison with power plant mills

Experimental conditions were set to mimic dust accumulations in power plant mills during standstill, using comparatively low gas flow rates. Fires are likely linked to shutdown and restart of mills, suggesting that long residence times and poor heat dissipation lead to ignition (compare Chapter 2.2). Under full load, up to 14 kg s$^{-1}$ of wood pellets and 20 kg s$^{-1}$ of pre-heated air pass through a mill [12]. Based on operator experience from the Danish CHP-plant Avedørevarket, it was estimated that fresh and partially ground pellets form an up to 50 mm thick layer on the mill table in operation, resulting in at least 50–100 kg of fuel present in the mills. The full fuel inventory is unknown, as their are also fine airborne particles in the mill. On shutdown, these would fall out of suspension and add to the fuel layer on the mill table or settle on other free surfaces in the mill. In comparison, experiments with sample mass between 10–40 g are scaled down by a factor of 2500–10 000.

Even with air fans shut off, there may be a draft through the mills, providing oxygen and possibly also contributing to cooling of settled dust accumulations. Scaling flowrates up from experimental conditions assuming constant velocity ($0.03 \text{ m s}^{-1}$) would give air flow rates of 0.1 kg s$^{-1}$ (at standard con-
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ditions, assuming a mill diameter of 2 m). This is orders of magnitude below
the air flow rates when the mill is in operation, and less than the sealing air
flow (compare [12]).

A.3.6.2. Diffusion limitations

Reaction rates increase exponentially with temperature, whereas diffusion
rates have a weaker temperature dependency. Reactions can therefore be-
come diffusion-limited due to lack of oxygen as reactions progress. Change
of concentration \( C \) with time by diffusion along a spatial coordinate \( r \) is given
by Fick’s second law:

\[
\frac{\partial C}{\partial t} = -D \cdot \frac{\partial^2 C}{\partial r^2} \quad (A.9)
\]

where \( D \) is the diffusion coefficient. The expression can be used to estimate
the rate at which oxygen is transported into the reaction zone. The criti-
cal case is diffusion from the ambient to the center of the sample \( (r = 0) \),
where symmetry is assumed. Replacing \( \partial C/\partial t \) by a molar consumption rate
of oxygen per volume \( (\hat{n}_{O_2}/V) \), and linearizing the spatial gradient:

\[
\hat{n}_{O_2,D} = -D \cdot \frac{C_{O_2}(r = 0) - C_{O_2}(r = r_{\text{max}})}{\Delta r^2} \cdot V \quad (A.10)
\]

Assuming all oxygen has been consumed at \( r = 0 \), this simplifies to

\[
\hat{n}_{O_2,D} = D \cdot \frac{C_{O_2}(r = r_{\text{max}})}{\Delta r^2} \cdot V \quad (A.11)
\]

where \( \Delta r \) is the critical length \( L \) of the problem. Further assuming that
the surrounding atmosphere behaves as a perfectly stirred reactor (i.e., no
boundary layer at the sample and no concentration gradients), the oxygen
concentration at \( r_{\text{max}} \) is equal to that of the ambient atmosphere \( (C_{O_{2,\text{amb}}}) \).
A power-law dependence between the diffusion coefficient and temperature
is assumed:

\[
D \propto T^{1.75} \quad (A.12)
\]

Temperature exponents for diffusion vary in the literature, but their range is
theoretically limited to 1.5–2.0 [169].

The rate of oxygen consumption can be calculated from the rate constant \( k \)
and the stoichiometric oxygen demand. Rate constants are modelled by an
Arrhenius expression, assuming an \( n \)-order reaction in oxygen. Conversion
$X$ of the solid material $s$ is described by:

$$\frac{dX_s}{dt} = k \cdot (1 - X_s)^{n_s} \cdot \left(\frac{p_{O_2}}{p_{ref}}\right)^{n_{O_2}} ; \quad k = k_0 \cdot \exp\left(\frac{E_a}{RT}\right)$$ (A.13)

where $p_{O_2}$ is the partial pressure of oxygen, divided by $p_{ref} = 1$ Pa for dimensional correctness. Reaction orders in the solid and in oxygen are given by $n_s$ and $n_{O_2}$, respectively. Stoichiometric oxygen demand is calculated by assuming a pseudo-reaction of the solid biomass:

$$C_xH_yO_z + \nu_{O_2}O_2 \rightarrow \nu_{CO_2}CO_2 + \nu_{CO}CO + \nu_{H_2O}H_2O$$ (A.14)

where $\nu_i$ are the stoichiometric coefficients of species $i$. The stoichiometric coefficient for oxygen can be calculated from the solid species composition ($C_xH_yO_z$), if a ratio between CO and CO$_2$ is assumed. The decrease in oxygen concentration depends on the amount of solid biomass, expressed by the bulk density $\rho_b$. For a known biomass composition $C_xH_yO_z$, this can be converted into a molar concentration $C_b$ via the molar mass $M$, $C = \rho / M$. The corresponding stoichiometric oxygen concentration is then $C_{O_2,stoich} = \nu_{O_2} \cdot C_b$.

Neglecting the effect of solid conversion on reactions (i.e., $n_s := 0$), and assuming $p_{O_2}$ to be constant (no oxygen depletion), the integral rate for complete conversion within a volume $V$ is given by

$$\dot{n}_{O_2,R} = C_{O_2,stoich} \cdot k_{O_2} \cdot V$$

$$= C_{O_2,stoich} \cdot k \cdot \left(\frac{p_{O_2}}{p_{ref}}\right)^{n_{O_2}} \cdot V$$ (A.15)

where $k_{O_2}$ contains the effects of temperature and oxygen partial pressure on the reaction rate. Both depletion of the solid as well as consumption of oxygen will slow down conversion, so that the above overestimates reaction rates.

Combining equations A.11 and A.15, the Damköhler-number is estimated by

$$Da = \frac{k_{O_2} C_{O_2,stoich} L^2}{DC_{O_2,amb}}$$ (A.16)

Parameters used in the estimate calculation are summarized in Table A.4, results are shown in Chapter 5, Fig. 5.2. Kinetic parameters were adapted from Chapter 4.
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Table A.4.: Parameters used in estimate calculations of transport limitations. Geometric parameters \((A_s, A_w, L)\) given by sample and oven geometry.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
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</tr>
</thead>
<tbody>
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<td>LHV</td>
<td>[MJ kg(^{-1})]</td>
<td>19.8</td>
</tr>
<tr>
<td>(\rho_b)</td>
<td>[kg m(^{-3})]</td>
<td>120</td>
</tr>
<tr>
<td>(\nu \text{CO}/\nu \text{CO}_2)</td>
<td>[-]</td>
<td>0.5</td>
</tr>
<tr>
<td>(k_0)</td>
<td>[s(^{-1})]</td>
<td>(1.04 \times 10^{-7})</td>
</tr>
<tr>
<td>(E_a)</td>
<td>[kJ mol(^{-1})]</td>
<td>130</td>
</tr>
<tr>
<td>(n_{O_2})</td>
<td>[-]</td>
<td>0.4</td>
</tr>
<tr>
<td>(n_s)</td>
<td>[-]</td>
<td>0</td>
</tr>
<tr>
<td>(D_{\text{ref}})</td>
<td>[m(^2) s(^{-1})]</td>
<td>(1.5 \times 10^{-5})</td>
</tr>
<tr>
<td>(T_{\text{ref}})</td>
<td>[K]</td>
<td>300</td>
</tr>
<tr>
<td>(y_{O_2})</td>
<td>[mol mol(^{-1})]</td>
<td>0.2</td>
</tr>
<tr>
<td>(p)</td>
<td>[Pa]</td>
<td>101325</td>
</tr>
<tr>
<td>(\varepsilon_s)</td>
<td>[-]</td>
<td>0.8</td>
</tr>
<tr>
<td>(\varepsilon_w)</td>
<td>[-]</td>
<td>0.8</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>[W m(^{-2}) s(^{-1})]</td>
<td>10</td>
</tr>
</tbody>
</table>

A.3.6.3. Heat transfer

Relative effects of self-heating and external heat transfer are estimated for different temperatures and temperature differences between sample (surface) and surroundings. Heat transfer appears both by convection between gas flow and sample \(\dot{Q}_\alpha\) and as radiation between oven wall and sample \(\dot{Q}_\varepsilon\):

\[
\dot{Q}_{\text{ext}} = \dot{Q}_\alpha + \dot{Q}_\varepsilon \tag{A.17}
\]

\[
\dot{Q}_\alpha = \alpha A_s (T_g - T_s) \tag{A.18}
\]

\[
\dot{Q}_\varepsilon = \sigma \varepsilon A_s (T^4_w - T^4_s) \tag{A.19}
\]

\[
\varepsilon = \left( \frac{1}{\varepsilon_s} + \frac{A_s}{A_w} \cdot \left( \frac{1}{\varepsilon_w} - 1 \right) \right)^{-1} \tag{A.20}
\]

where \(\alpha\) is the heat transfer coefficient, \(\varepsilon\) the emissivity coefficient, \(\varepsilon_s\) and \(\varepsilon_w\) the emissivities of sample and oven wall, respectively, \(\sigma\) the Stefan-Boltzmann constant, and \(A_s\) and \(A_w\) the surface areas of sample and oven wall.

Heating rates from reaction are based on the above simple reaction model.
(eq. A.13), again neglecting the effects of solid conversion on reaction rates:

$$\dot{Q}_R = \Delta H_R C_s V k \cdot \left( \frac{p_{O_2}}{p_{ref}} \right)^{n_{O_2}} \tag{A.21}$$

where $\Delta H_R$ is the heat of reaction in J mol$^{-1}$ and $C_s \cdot V$ is the amount of biomass. Heat of reaction is estimated based on the lower heating value (LHV) of pine wood, corrected for partially incomplete conversion of carbon to CO instead of CO$_2$.

Parameters used in the estimate calculation are summarized in Table A.4, results are shown in Chapter 5, Fig. 5.3. The value of the activation energy $E_a = 130$ kJ mol$^{-1}$ gives a steep increase of reaction heating rate $\dot{Q}_R$ with temperature. At lower temperatures (300–350 K), heat release rates estimated are much lower (ranging from $2.5 \times 10^{-7}$ mW g$^{-1}$ to $4.3 \times 10^{-4}$ mW g$^{-1}$) than those found in the literature [81, 82, 103] (0.025–20 mW g$^{-1}$). These authors however also find much lower activation energies (55–80 kJ mol$^{-1}$). Discrepancies may arise from assuming mass loss rate and heat release to be proportional or from extrapolating rates to low temperatures. Kinetic parameters were fit to data for >423 K. As discussed in Chapter 4, the ‘global’ reaction rate may miss low temperature effects.

The estimated heat transfer coefficient ($\alpha = 10$ W m$^{-2}$s$^{-1}$) is an upper bound. For gas temperatures between 310–650 K, calculated Reynolds-numbers are within a range of Re = 30–50. Nusselt-numbers fall within Nu = 4–6 (see Appendix A.4.4 for applicable correlations), resulting in $\alpha = 5-10$ W m$^{-2}$s$^{-1}$.

At higher temperatures, from $\approx 390$ K upwards, radiative heat transfer exceeds that by convection. Ratios $Q_r/Q_a$ increase from 1.1 at 400 K to 3.8 at 600 K.

### A.3.7. Additional experimental data

#### A.3.7.1. Effect of heating rate

External heating rate influences the temperature distribution within the sample, and thus the production of CO and CO$_2$, during the external-heating-controlled phase (Fig. A.24). Nominal oven heating rates were set to 1, 5 and 10 K/min. In the pulse ignition experiment, the sample was rapidly inserted into the preheated oven. All other parameters were equal in these experiments (nominal final oven temperature 503 K, 20% oxygen). From the dashed lines representing the oven temperature in Fig. A.24a, it is apparent that the oven could not completely follow the preset temperature curve. Deviations from the ideal behavior are especially apparent for the 5 K/min and
Figure A.24.: Pine (50–200 µm) heated to 503 K nominal oven temperature at different heating rates, in 20 % oxygen atmosphere. Solid lines on top left are sample center temperature, dashed lines oven temperatures.
10 K/ min experiments. Heat released during burn out of the sample also led to a temporary increase of the oven temperature over its preset value at or near the end of each experiment.

Fig. A.24b shows temperature differences between sample center and oven. Data are plotted over sample center temperature, which can be understood as a reaction progress variable. A negative temperature difference $\Delta T < 0$ indicates a net heat transfer from the surroundings to the sample. Thermal runaway can be identified by curves approaching a slope of $\Delta T/T \approx 1$, i.e., heating rates of the sample are much faster than those of the oven. In comparison, a constant difference between sample center and oven shows that both experience the same heating rate. As apparent in Fig. A.24b, the onset temperature of thermal runaway is practically independent of heating rate. Data from all experiments fall on the same line for temperatures $>520$ K.

Temperature distribution within the sample can be seen in Fig. A.24c by comparing temperature in the sample boundary to those in the sample center. For better comparison, the dashed line marks equal boundary and center temperature values. Heating occurs outside-in up to $\approx 470-490$ K. The spread between boundary and center temperatures is larger for higher heating rates.

A.3.7.2. Conversion in subcritical experiments

Data from subcritical experiments are summarized in Table A.5 and Fig. A.25. Final oven temperature, oxygen volume fraction at the oven inlet and total gas flow rate were the main parameters set in the experiments. Oven temperatures and oxygen concentrations frequently deviated from their respective setpoint values. Duration of the experiment ($t_f$) was not varied systematically, but analysis of several experiments showed this parameter to influence conversion (Figs. A.25a, A.25c and A.25e). Results at equal nominal oven temperature and 20% oxygen suggest a linear trend between total conversion (based on mass loss measurement) and duration of the experiment (Fig. A.25a). Carbon conversion (based on time-integrated measurements of CO and CO$_2$) follows a similar trend for the 500 K (Fig. A.25c) experiments, but large scatter among the data is seen for 495 K experiments. For specific oxygen consumption (Fig. A.25e), there appears to be even broader scatter in the 495 K experiments.

Corrected for the duration of the experiment (i.e., $X/t_f$, which corresponds to an integral conversion rate), total conversion correlates with final oven temperature (Fig. A.25b). Additionally, lower oxygen concentrations leads to lower conversion. For carbon conversion to CO and CO$_2$ (Fig. A.25d) and
Table A.5: Subcritical experiments pine by nominal oxygen concentration. Size: c(coarse) is 600–1000 µm, f(fine) is 50–200 µm sieve fraction.

<table>
<thead>
<tr>
<th>% O₂</th>
<th>[%]</th>
<th>[L/min]</th>
<th>[min]</th>
<th>[K]</th>
<th>[K]</th>
<th>[K]</th>
<th>[g]</th>
<th>[g]</th>
<th>[g]</th>
<th>[g]</th>
<th>[%]</th>
</tr>
</thead>
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<td>6.08</td>
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<td>0.295</td>
<td>1.08</td>
<td>1.82</td>
<td>0.93</td>
<td>0.19</td>
<td>8.0</td>
</tr>
<tr>
<td>19%</td>
<td>16.4</td>
<td>4.70</td>
<td>0.055</td>
<td>0.53</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>8.0</td>
</tr>
<tr>
<td>17%</td>
<td>18.2</td>
<td>4.93</td>
<td>0.045</td>
<td>0.43</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
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</tr>
<tr>
<td>16%</td>
<td>19.3</td>
<td>5.00</td>
<td>0.060</td>
<td>0.70</td>
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<td>0.70</td>
<td>0.70</td>
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<td>0.70</td>
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<tr>
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<td>0.80</td>
<td>0.80</td>
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<tr>
<td>13%</td>
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<td>0.80</td>
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<td>0.80</td>
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<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Note: Table A.5: Support data for experiments pine by nominal oxygen concentration. Size: c(coarse) is 600–1000 µm, f(fine) is 50–200 µm sieve fraction.
Figure A.25.: Effect of experiment duration and temperature on total conversion $X_{\text{tot}}$, carbon conversion $X_C$ and specific oxygen consumption $X_O$ in subcritical heating experiments. Temperatures are measured final oven temperatures. Data in Table A.5.
specific oxygen consumption rates (Fig. A.25f), no comparable trends are found.

Integral conversion rates also do not appear to be correlated among each other, Fig. A.26. Conversion of the total organic fraction and conversion to CO and CO\(_2\) is likely uncorrelated because of competing reactions of fuel carbon to e.g. volatiles and tars. Apparently, these pyrolytic reactions do not occur at the same rates as carbon oxidation reactions. Secondly, CO and CO\(_2\) are themselves possible pyrolysis products. Possibly, consumption of oxygen and formation of CO and CO\(_2\) are unrelated for the same reason. Additionally, oxygen is also consumed in oxidizing fuel hydrogen.

### A.3.7.3. Sample mass

Figure A.27 shows the time-temperature history of the 19 g, coarse pine experiment. Note that the oven temperature briefly deviates from the programmed heating rate. This was not seen in other experiments, and may be due to a temperature controller malfunction.

Combined emission rates of CO and CO\(_2\) increase exponentially with temperature and show a broad scatter, Fig. A.28. Scaling the same data by initial sample mass lets most measurements collapse onto the same curve, Fig. A.29. Differences between the 8 g fine sample and the other fine samples may be due to a different bed shape, as that sample did not completely

Figure A.26.: Integral conversion rates of carbon and the total organic fraction, as well as integral specific oxygen consumption are uncorrelated for subcritical experiments
Figure A.27.: Temperature time history of the 19 g, coarse pine experiment. Note the brief increase in oven temperature above the programmed constant heating rate around 70 minutes (arrow). Temperature spikes around 320–350 minutes are possibly secondary ignition of char.

fill the sample holder. This would however not explain why coarse samples 15 g and 21 g follow the same trend as the fine samples, while 18 g and 19 g (coarse) do not.

Individually, trends of CO and CO$_2$ show the same qualitative behavior as the sum of both gases (compare Figs. A.30 and A.31 with Fig. 5.7). Most notably, CO emissions are always lower than those of CO$_2$, and both show a similar spread at any given temperature.

**A.3.7.4. Oxygen concentration**

Time-series data for the coarse pine experiments reported in Table 5.3 is shown in Figs. A.32 and A.33.

Images of samples before and after experiments are seen in Figure A.34. Images Fig. A.34a and A.34a show a pine wood sample with 50–200 µm particle size before and after the experiment. The sample as a whole contracts towards the center (note the gaps between the sample char and the sample holder walls in Fig. A.34a: ca. 10 mm on the left and 7 mm on the right), but otherwise retains its shape.
Figure A.28.: Combined CO and CO\(_2\) release at onset. Unscaled data.

Figure A.29.: Combined CO and CO\(_2\) release at onset. Mass-scaled data.
Figure A.30.: CO release scaled by sample mass

Figure A.31.: CO$_2$ release scaled by sample mass
Figure A.32.: Oxygen depletion depending on inlet oxygen concentration and total volumetric flowrate

Figure A.33.: Temperature difference between sample center and oven depending on inlet oxygen concentration and total volumetric flowrate
Figure A.34.: Pre- and post-burnout images of pine samples at different oxygen concentrations (compare Table 5.3). Distance between the front and back plates of the sample basket is 150 mm (inside).
A.3.7.5. Materials

Time-series data for temperature and gas composition for beech, sunflower and wheat are shown in Figures A.35 and A.36. The corresponding data for pine are found in Chapter 5, Figures 5.4 and 5.5. Note that timescales may vary between different experiments.

Corresponding data for experiments with cellulose, lignin and xylan are found in Figures A.37 and A.38. Experiments for isolated components were run to higher final oven temperatures than those of the native biomasses (623 K instead of 573 K).

Ratios of CO to CO$_2$ were additionally evaluated in all experiments. Fig. A.39 shows data for beech, pine, sunflower husk pellets and wheat straw, results for cellulose, lignin and xylan are found in Fig. A.40.
Figure A.35.: Data from fixed bed oxidation experiments for beech, sunflower husk pellets and wheat straw. 20% oxygen, heated at 1 K/min to 573 K (nominal values). Data for pine: see Figs. 5.4 and 5.5.
APPENDIX A.3

Figure A.36.: Data from fixed bed pyrolysis experiments for beech, sunflower husk pellets and wheat straw. 0% oxygen, heated at 1 K/min to 573 K (nominal values). Data for pine: see Figs. 5.4 and 5.5.
Figure A.37.: Data from fixed bed oxidation experiments for cellulose, lignin and xylan. 20% oxygen, heated at 1 K/min to 623 K (nominal values).
Figure A.38.: Data from fixed bed pyrolysis experiments for cellulose, lignin and xylan. 0% oxygen, heated at 1 K/min to 623 K (nominal values).
Figure A.39.: CO/CO₂-ratio for different biomasses under oxidizing conditions (top) and pyrolysing conditions (bottom). Discontinuities/overlaps due to switching analyzer data range from ‘low’ to ‘high’ range. Experiments were run at 1 K/ min heating rate from ambient to 573 K nominal oven temperature. Compare Table 5.4.
Figure A.40.: CO/CO$_2$-ratio for cellulose, lignin and xylan under oxidizing conditions (top) and pyrolysing conditions (bottom). Discontinuities/overlaps due to switching analyzer data range from ‘low’ to ‘high’ range. Experiments were run at 1 K/min heating rate from ambient to 623 K nominal oven temperature. Compare Table 5.5.
A.4. Modelling equations

A.4.1. Derivation of the model equations

The integral form of the balance equations is given below, where eq. A.22 is the mass balance for solid species $i$, eq. A.23 the species balance in the interstitial gas phase, eq. A.24 the heat balance in the dust bed (combining solid and interstitial gas), eq. A.25 the species balance in the bulk gas, and eq. A.26 the heat balance in the bulk gas phase. For each cell in the domain, the local change is due to flux over the surface of the cell and local sources.

\begin{align*}
\int_V \frac{\partial \rho_{s,i}}{\partial t} dV &= \dot{m}_{R,s,i} \quad (A.22) \\
\int_V \phi \frac{\partial C_{g,i}}{\partial t} dV &= - \int_A \phi D \frac{\partial C_{g,i}}{\partial r} dA + \int_A \phi C_{g,i} u dA + \dot{n}_{R,g,i} \quad (A.23) \\
\int_V \frac{\partial T}{\partial t} dV &= - \int_A \frac{\lambda}{\rho_s c_{p,s} + \rho_g c_{p,g}} \frac{\partial T}{\partial r} dA + \frac{\dot{Q}_R}{\rho_s c_{p,s} + \rho_g c_{p,g}} \quad (A.24) \\
\int_V \frac{\partial C_{g,i}}{\partial t} dV &= - \int_A D \frac{\partial C_{g,i}}{\partial r} dA + \int_A C_{g,i} u dA + \dot{n}_{g,i,in} - \dot{n}_{g,i,out} \quad (A.25) \\
\int_V \frac{\partial T_g}{\partial t} dV &= - \int_A \frac{1}{\rho_g c_{p,g}} \left( \dot{H}_{g,in} - \dot{H}_{g,out} + \dot{H}_{s-g} + \int_A \dot{Q}_a dA \right) \quad (A.26)
\end{align*}

Equations A.23 and A.25 differ only in the source terms/boundary conditions and the porosity (dust bed: $\phi < 1$, bulk gas: $\phi = 1$). Sums eq. 6.3–6.5 are used to close the system of equations. In the above, the left-hand sides are the change within the volume. The $\partial / \partial r$-terms are diffusive transport, $u dA$-terms are advective transport over the cell surface and the terms with a dot are source/sink-terms. Mass and species balances can be set up globally as well as individually for all species. In the global balances, the net rate of mass production is zero. Additionally, the net diffusion of gaseous species is zero. Bulk movement of the gas phase is covered in the advective transport term. The individual terms in equations A.22 to A.26 are discussed further below.

**Mass balance**  The reacting material (e.g. a bed of settled dust particles) is porous on a macroscopic level, and can therefore be split into an actual solid phase and the interstitial gas phase, so that $\rho = \rho_s + \rho_g$. The mass balance
can be split into a balance of the solid and the interstitial gas (where \( j \neq i \)):

\[
\int_V \frac{\partial \rho_s}{\partial t} dV = \sum_i \dot{m}_{R,s,i} \tag{A.27}
\]

\[
\int_V \frac{\partial \rho_g}{\partial t} dV = \sum_j M_j \cdot \left( \int_A -D \frac{\partial C_{g,j}}{\partial r} dA + \int_A C_{g,j} u dA + \dot{n}_{R,g,j} \right) \tag{A.28}
\]

In the above, \( \dot{m}_{R,s,i} \) is a source/sink term to account for the reaction of solids \( i \), \( M_i \) the molar mass of species \( i \), and the term in brackets is a gaseous species balance (eq. A.23).

**Heat balance** Change in enthalpy in the dust bed is due to conduction, advection and reaction within the model domain; as well as convection, radiation and conduction at interfaces. In the simplified form of the heat balance (eq. A.24), temperature differences between the incoming stream and the cell it enters are neglected. This must then be compensated for by an increased diffusive heat transfer (i.e. conduction in the solid). This assumption holds for small Péclet numbers (systems with fast thermal diffusion and slow advective transport), where Pe is given by:

\[
Pe = \frac{u \cdot L}{a} \tag{A.29}
\]

The assumption simplifies the implementation of the energy balance, as the flow velocity \( u \) does not need to be evaluated. It also avoids implementing an upwind scheme to solve the advective transport.

The enthalpy exchange bewteen dust bed and bulk gas phase can be approximated by:

\[
\dot{H}_{s-g} = \int_V \sum_j M_j \left( \frac{\partial C_{g,j}}{\partial t} dV - \dot{n}_{R,g,j}^{\text{w}} \right) \cdot c_{p,g} \cdot T_V dV \tag{A.30}
\]

where the term in brackets is the net change in concentration of species \( j \) minus its net volumetric rate of production (i.e. the term in brackets is the advective transport of the species). Since the sum of all species is considered, the diffusion terms cancel (no net diffusion). The advective transport stream is multiplied with the specific heat capacity and temperature of the volume it originates from, which is integrated over the volume of the dustbed. This assumes that the net stream of gas is always outwards and that convective heat transfer within the porous solid is negligible, i.e. the gas stream flows out from the volume element it originates from without exchanging heat with the bed volume it passes through.
Gaseous species balance  In the species balance (eq. A.23), the advective term appears when a pressure gradient exists. The velocity of the gas flow through the dust bed can then be modelled by Darcy’s law:

\[ u = -\frac{\kappa}{\eta} \cdot \frac{dp}{dr} \]  

(A.31)

where \( \kappa \) is the permeability of the bed in units of \([m^2]\) and \( \eta \) the dynamic viscosity of the gas in \([Pa \cdot s]\). In this model, pressure gradients arise only from reactions, i.e. release of gaseous products and changes in temperature. Using the ideal gas law and Dalton’s law of partial pressures, pressure can be substituted by

\[ p = \frac{C_{g,j}}{y_{g,j}} RT \]  

(A.32)

where \( y_j \) is the mole fraction of component \( j \). Substituting the above directly gives

\[ \int_A C_{g,j} u \, dA = -\int_A C_{g,j} \frac{\kappa}{\eta} \cdot \frac{d}{dr} \left( \frac{C_{g,j}}{y_{g,j}} RT \right) \, dA \]  

(A.33)

which has the form of a diffusion flux when used in equation A.23. The concentration \( C_j \) outside the differential is evaluated at the surface of the cell. The balance equation then reads:

\[ \int_V \frac{\partial C_{g,j}}{\partial t} \, dV = \int_A -D \frac{\partial C_{g,j}}{\partial r} \, dA - \int_A C_{g,j}(A) R \frac{\kappa}{\eta} \cdot \frac{\partial}{\partial r} \left( \frac{C_{g,j}}{y_{g,j}} T \right) \, dA + \dot{n}_{R,g,j} \]  

(A.34)

The advantage of using the above expression is that it is then possible to solve the species balance for each species \( j \) separately. Thereby, it can be avoided to calculate the pressure field as a function of the sum of all concentrations, and to solve equations describing the flow field.

A.4.2. Outflow boundary condition

The outflow is evaluated based on inflow, production (release) of gaseous species and accumulation within the modelling domain. It is formulated on a molar basis in the following. The accumulation is given as:

\[ \frac{dn}{dr} = \dot{n}_{\text{in}} + \dot{n}_{\text{s-g}} - \dot{n}_{\text{out}} \]  

(A.35)
Assuming steady state of inflow (index in), outflow (out) and production terms (s – g), this can be integrated over a timestep $\Delta t$ and rearranged:

$$n(t_0 + \Delta t) = n(t_0) + \dot{n}_{\text{in}} + \dot{n}_{s-g} - \dot{n}_{\text{out}} \tag{A.36}$$

Using the ideal gas law and keeping the volume of the bulk gas constant,

$$n \frac{T}{p} = \frac{V}{R} = \text{const.} \tag{A.37}$$

it follows that

$$n(t_0 + \Delta t) = n(t_0) \cdot \frac{T(t_0)}{T(t_0 + \Delta t)} \frac{p(t_0 + \Delta t)}{p(t_0)} \tag{A.38}$$

Combining equations A.36 and A.38 and rearranging:

$$\dot{n}_{\text{out}} = \dot{n}_{\text{in}} + \dot{n}_{s-g} - \frac{V}{R \Delta t} \left( \frac{p(t_0 + \Delta t)}{T(t_0 + \Delta t)} - \frac{p(t_0)}{T(t_0)} \right) \tag{A.39}$$

In this equation, the pressure $p(t_0 + \Delta t)$ is set as boundary condition $p_{BC}$. The value of $p(t_0)$ is evaluated from total concentration and temperature, using the ideal gas law. The outflow condition then reads:

$$\dot{n}_{\text{out}} = \dot{n}_{\text{in}} + \dot{n}_{s-g} - \frac{V}{R \Delta t} \left( \frac{p_{BC}}{T(t_0 + \Delta t)} - \sum_j C_j(t_0) \cdot \frac{R}{\sum} \right) \tag{A.40}$$

A.4.3. Heat transfer by radiation

$\varepsilon$ is calculated as

$$\varepsilon = \left( \frac{1}{\varepsilon_s} + \frac{A_s}{A_w} \cdot \left( \frac{1}{\varepsilon_w} - 1 \right) \right)^{-1} \tag{A.41}$$

Indices s and w refer to solid and wall, respectively. Note that this calculation does not take the geometry of the problem into account, i.e. how the two surfaces $A_s$ and $A_w$ are oriented. The above equation is strictly only valid if the two surfaces are parallel to each other. Radiation of the gas body is neglected.

A.4.4. Heat transfer by convection

The heat transfer coefficient $\alpha$ can be calculated from a Nusselt-correlation:

$$\alpha = \text{Nu} \cdot \frac{\lambda_g}{L_{\text{char}}} \tag{A.42}$$
using the gas-phase thermal conductivity $\lambda_g$ and a characteristic length $L_{\text{char}}$. The choice of a characteristic length $L_{\text{char}}$ depends on the geometry of the problem. The Nusselt number $\text{Nu}$ is itself a function of the dimensionless Reynolds, Prandtl, and Grashof numbers, describing the geometry, material properties and surrounding conditions. The Reynolds number is the ratio of inertial to viscous forces:

$$\text{Re} = \frac{u_g \cdot L_{\text{char}}}{\bar{v}_g} \quad (A.43)$$

The Prandtl number $\text{Pr}$ is the ratio of viscous diffusivity to thermal diffusivity.

$$\text{Pr} = \frac{\nu}{\alpha} \quad (A.44)$$

where the thermal diffusivity $\alpha = \lambda / (\rho c_p)$.

The Grashof number $\text{Gr}$ is used to describe the relative influence of forced and natural convection in heat transfer:

$$\text{Gr} = \frac{g \cdot \beta \cdot (T - T_\infty) \cdot L_{\text{char}}}{\bar{\nu}^2} \quad (A.45)$$

where $\beta$ is the thermal expansion coefficient ($\approx 1/T_\infty$), $T$ the temperature of wall or solid, $T_\infty$ the bulk gas temperature, and $\bar{\nu}$ the kinematic viscosity.

In case of forced convection, usually laminar and turbulent flows are distinguished as this influences the heat transfer. Rough calculations based on settings used in the validation experiments show a low Reynolds-number flow ($\text{Re} < 100$), indicating that convective heat transfer is likely dominated by free convection under most conditions.

**Heat transfer on the outside of slender cylinders** The samples used in the experiments had the shape of a long cylinder, with length to diameter ratio $l/d = 5$. The Nusselt number for *free convection* on the sample wall can be calculated by [205]

$$\text{Nu}_{\text{free}} = \left(0.6 + 0.387 \cdot (\text{Pr} \cdot \text{Gr} \cdot f_1(\text{Pr}))^{1/6}\right)^2 \quad (A.46)$$

where $L_{\text{char}} = d$ and $f_1(\text{Pr})$ evaluates to 0.326 over the range of interest. The Nusselt number for *forced convection* of a longitudinal flow around a cylinder is described by [19]

$$\text{Nu}_{\text{forced}} = \frac{0.55}{K^{0.5}} + \frac{0.95}{K^{0.1}} \quad (A.47)$$
where $K$ is a curvature parameter

$$K = \frac{\vec{v} \cdot l}{(d/2)^2 \cdot u} \quad (A.48)$$

The total Nusselt number is found by superimposing forced and free convection:

$$Nu = \left( Nu_{\text{forced}}^3 + Nu_{\text{free}}^3 \right)^{1/3} \quad (A.49)$$

**Heat transfer on the top of a horizontal flat surface** Free convection is driven by buoyancy forces, and appears on top of a surface warmer than its surroundings. Depending on temperature conditions and material properties, one of two equations are used [19], where

$$Nu_{\text{free}} = 0.766 \cdot (Pr \cdot Gr \cdot f_2(Pr)^{0.2}; \quad \text{for } Pr \cdot Gr \cdot f_2(Pr) < 7 \times 10^4 \quad (A.50)$$

$$Nu_{\text{free}} = 0.15 \cdot (Pr \cdot Gr \cdot f_2(Pr)^{1/3}; \quad \text{for } Pr \cdot Gr \cdot f_2(Pr) \geq 7 \times 10^4 \quad (A.51)$$

where $f_2(Pr)$ is 0.401 over the range of parameters considered.

Forced convection appears only in the wake of the solid body, since its lateral surfaces are assumed adiabatic in the 1D-model. Correlations for this heat transfer configuration are not very common, and are typically limited to high Reynolds-number flows. Forced convection on the wake of bluff bodies appears as secondary flow structures (eddies, vortices). These are a result of flow separation, which is much more pronounced in high velocity flows.

An upper bound for convective heat transfer can be found by assuming a flow parallel to a flat surface. For this configuration, Nusselt-correlations are readily found [19]. For laminar flows,

$$Nu_{\text{lam}} = 0.664 \cdot Re^{0.5} \cdot Pr^{1/3} \quad (A.52)$$

for turbulent flows,

$$Nu_{\text{turb}} = \frac{0.037 \cdot Re^{0.8} \cdot Pr}{1 + 2.443 \cdot Re^{-0.1} \cdot (Pr^{2/3} - 1)} \quad (A.53)$$

where the total Nusselt-number for forced flow is found by superposition:

$$Nu_{\text{forced}} = \left( Nu_{\text{lam}}^2 + Nu_{\text{turb}}^2 \right)^{1/2} \quad (A.54)$$
and the total Nusselt-number combining free and forced convection from

$$\text{Nu} = \left( \text{Nu}_{\text{forced}}^3 + \text{Nu}_{\text{free}}^3 \right)^{1/3} \quad (A.55)$$

**Heat transfer on the inside walls of the enclosure** Similarly, the Nusselt-correlation for the inside wall can be found. For want of a correlation describing free convection inside a hollow cylinder, the following equation for a vertical plate [206] is used:

$$\text{Nu}_{\text{free}} = \left( 0.825 + 0.387 \cdot (\text{Pr} \cdot \text{Gr} \cdot f_3(\text{Pr}))^{1/6} \right)^2 \quad (A.56)$$

where $L_{\text{char}} = d$ and $f_3(\text{Pr})$ evaluates to $0.354$ over the range of interest. In the experiments carried out, free convection likely contributes only a small part to the overall heat transfer, so errors made in this approximation should not have a profound effect on the overall calculation.

For forced convection, the enclosure is treated as an empty pipe. The flow velocity is however corrected for the reduced cross-section, which is partly blocked by the sample. The following correlations are taken from [19]. $d$ refers to the inner diameter of the tube oven, $l$ to its length. Laminar flow ($\text{Re} < 2300$) is described by

$$\text{Nu}_{\text{lam}} = \left( 3.66^3 + 0.7^3 + \left( 1.165 \cdot \left( \frac{\text{Re} \cdot \text{Pr} \cdot d}{T} \right)^{1/3} - 0.7 \right)^3 \right)^{1/3} \quad (A.57)$$

and turbulent flow ($\text{Re} > 10000$) by

$$\text{Nu}_{\text{turb}} = \frac{X \cdot \text{Re} \cdot \text{Pr}}{1 + 12.7 \cdot X^{1/2} \cdot (\text{Pr}^{2/3} - 1)} \cdot \left( 1 + \frac{1}{3} \cdot \left( \frac{d}{T} \right)^{2/3} \right), \quad (A.58)$$

$$X = \frac{1}{8} \cdot (1.8 \cdot \log(\text{Re}) - 1.5)^{-2} \quad (A.59)$$

For the transitional region, $\text{Nu}_{\text{trans}}$ is defined by

$$\text{Nu}_{\text{trans}} = (1 - Y) \cdot \text{Nu}_{\text{lam}}(\text{Re} = 2300) + Y \cdot \text{Nu}_{\text{turb}}(\text{Re} = 10000), \quad (A.60)$$

$$Y = \frac{\text{Re} - 2300}{10000 - 2300} \quad (A.61)$$

Again, the total of forced and free convection effects are calculated by choosing the appropriate $\text{Nu}_{\text{forced}}(\text{Re})$ from the above equations and using

$$\text{Nu} = \left( \text{Nu}_{\text{forced}}^3 + \text{Nu}_{\text{free}}^3 \right)^{1/3} \quad (A.62)$$
APPENDIX A.4

A.4.5. Elemental balances

Oxidation reactions have the form R6.1. Stoichiometric coefficients can be calculated from:

\[ y_C = y_{CO} + y_{CO_2} \]  \hspace{1cm} (A.63)

\[ y_H = \frac{1}{2} y_{H_2O} \]  \hspace{1cm} (A.64)

\[ y_{O_2} = - \left( \frac{y_C}{1 + \left( \frac{y_{CO}}{y_{CO_2}} \right)} + \frac{1}{2} \left( \frac{y_C}{y_{CO_2}/y_{CO}} \right) + \frac{y_H}{4} - \frac{y_O}{2} \right) \]  \hspace{1cm} (A.65)

The above system of three equations for four unknowns can be solved by choosing a ratio \( y_{CO}/y_{CO_2} \), which is then a modelling parameter. CO was measured in larger quantities in the fixed bed experiments than could be attributed to pyrolysis alone.

Pyrolysis reactions (R6.2) require more parameters to define the product gas composition. By defining the ratios \( y_{gas}/y_{vol} \), \( y_{CO}/y_{CO_2} \) and \( y_{H_2O}/y_{CO_2} \), the element balance for oxygen (eq. A.66) can be solved.

\[ y_{CO_2} = \frac{y_{O}}{2 + \frac{y_{CO}}{y_{CO_2}} + \frac{y_{H_2O}}{y_{CO_2}}} \]  \hspace{1cm} (A.66)

\[ y_{CO} = \frac{y_{gas}/y_{vol} \cdot y_{CO}/y_{CO_2} \cdot y_{CO}}{y_{CO_2}} \]  \hspace{1cm} (A.67)

\[ y_{H_2O} = \frac{y_{gas}/y_{vol} \cdot y_{H_2O}/y_{CO_2} \cdot y_{CO}}{y_{CO_2}} \]  \hspace{1cm} (A.68)

Solution of the element balances for carbon, hydrogen and oxygen then gives the composition of the volatile pseudo-species:

\[ y_{C,VOL} = y_{fuel,C} - y_{CO_2} - y_{CO} \]  \hspace{1cm} (A.69)

\[ y_{H,VOL} = y_{fuel,H} - 2 \cdot y_{H_2O} \]  \hspace{1cm} (A.70)

\[ y_{O,VOL} = y_{fuel,O} - 2 \cdot y_{CO_2} - y_{CO} - y_{H_2O} \]  \hspace{1cm} (A.71)

Species released by pyrolysis of biomass are tars, hydrocarbons, as well as hydrogen, CO, CO\(_2\) and water vapor. Several authors [123, 124, 126, 127, 190-192] report product gas composition from pyrolysis or smoldering oxidation of different biomass materials. Data reported in the literature are however difficult to compare, as analysis techniques and type of data reported vary. A simplified approach is used in this model, where all organic volatiles and tars are considered a single species, and only gases that also
originates from combustion (CO, CO$_2$ and water vapor) are tracked individually. The ratio $\gamma_{\text{gas}}/\gamma_{\text{vol}}$ defines how much of the oxygen in the biomass ($y_O$) forms CO, CO$_2$ or water vapor. Distribution of those three gases is calculated from the elemental composition ($y_C$, $y_H$, $y_O$) and the modelling parameters $\gamma_{\text{CO}}/\gamma_{\text{CO}_2}$ and $y_{\text{H}_2\text{O}}/\gamma_{\text{CO}_2}$. Values used in the model are summarized in Table 6.3. The remaining carbon, hydrogen and oxygen form tars and organic volatiles (e.g. hydrocarbons, aldehydes, phenolic- and furan-based compounds [123, 124, 126, 127, 190–192]), which are modelled as a lumped species. Accurately predicting off-gas composition is not a key aspect of the model, and this simplified approach is therefore deemed sufficient.

## A.5. Model implementation

The following indices appear as subscripts or superscripts in the following:

- $i$ - species
- $j$ - species, where $i \neq j$
- $m$ - cell
- $r$ - reaction
- $t$ - time

The calculation algorithm is seen in Fig. A.41.

### A.5.1. Discretization

The model is discretized in space using a finite volume method. State and material properties are uniform within one cell, and quantities at the interface between two cells are evaluated by linear interpolation. In the following, superscript indices refer to timesteps and subscripts to cells, where

- $m$ is a cell
- $m-1$ its inward or bottom neighbor
- $m+1$ its outward or top neighbor
- $m-$ the interface between $m$ and $m-1$
- $m+$ the interface between $m$ and $m+1$
- $t$ the current time
- $t+1$ the next timestep

Solid cells for which both neighbors are also solids are called *internal cells* in the following. Solid cells for which only one neighbor is also a solid are
Figure A.41.: Model calculation algorithm (simplified). Steps within the dashed lines are carried out at each inner iteration.
boundary cells. For the innermost cell, either a wall or a symmetry boundary condition is applied, depending on the geometry. For the outermost solid cell, the boundary condition is an interface with the bulk gas phase (mass and heat transfer) and with a non-contacting wall (radiative heat transfer). The bulk gas phase is represented by a single cell.

Spatial gradients appear in the balance equations (eq. A.22 – A.26). The discretization of these $\partial/\partial r$-term depends on the geometry (Fig. 6.2): For a flat disk, i.e. a planar surface (Fig. 6.2c), the gradients are

$$\left. \frac{\partial}{\partial r} \right|_{m-} = \frac{1}{r_m - r_{m-1}} \quad \text{and} \quad \left. \frac{\partial}{\partial r} \right|_{m+} = \frac{1}{r_{m+1} - r_m} \quad (A.72)$$

For a cylinder shell, i.e. a surface curved in one dimension (Fig. 6.2b), the spatial gradients are:

$$\left. \frac{\partial}{\partial r} \right|_{m-} = \frac{1}{r_m} \cdot \log \left( \frac{r_m}{r_{m-1}} \right) \quad \text{and} \quad \left. \frac{\partial}{\partial r} \right|_{m+} = \frac{1}{r_m} \cdot \log \left( \frac{r_{m+1}}{r_m} \right) \quad (A.73)$$

For spheres (Fig. 6.2a), the gradients are:

$$\left. \frac{\partial}{\partial r} \right|_{m-} = \frac{1}{r_m^2} \cdot \left( \frac{1}{r_{m-1}} - \frac{1}{r_m} \right) \quad \text{and} \quad \left. \frac{\partial}{\partial r} \right|_{m+} = \frac{1}{r_m^2} \cdot \left( \frac{1}{r_m} - \frac{1}{r_{m+1}} \right) \quad (A.74)$$

In the above equations, $r_m, r_{m-1}, r_{m+1}$ are the midpoint coordinates and $r_{m-}, r_{m+}$ are the interface coordinates. The following notation will be used to refer to all geometries:

$$\frac{1}{(\Delta r)_{m-}} = \left. \frac{\partial}{\partial r} \right|_{m-} \quad \text{and} \quad \frac{1}{(\Delta r)_{m+}} = \left. \frac{\partial}{\partial r} \right|_{m+} \quad (A.75)$$

where the appropriate terms from either eq. A.73, A.72 or A.74 are used in the calculation. The transport coefficients $\lambda$ and $D$ at cell interfaces are evaluated by averaging the midpoint values of the adjacent cells.

**A.5.1.1. Mass balance**

Integrating the solid mass balance eq. A.22 for each solid species $i$ and discretizing in time gives

$$\frac{\rho_{i,m}^{(t+1)} - \rho_{i,m}^{(t)}}{\Delta t} \cdot V_m = \sum_{r} \left. m_{R,r,i} \right|_{m} \quad (A.76)$$
which can be rearranged to give the new densities:

\[
\rho_{i,m}^{(t+1)} = \sum_r \dot{m}_{R,r,i} \left| \frac{\Delta t}{V_m} \right| + \rho_{i,m}^{(t)} \tag{A.77}
\]

The total solid density is found by summing over all species densities, \( \rho_{m,s}^{(t+1)} = \sum_i \rho_{m,i}^{(t+1)} \). Since no solid mass is transported into or out of the solid domain, the above applies to all solid cells (internal and boundary cells).

### A.5.1.2. Heat balance

**Internal cells** Integrating over volume and surfaces in equation A.24 for internal cells yields:

\[
\frac{\partial T}{\partial t} \cdot V_m = -\frac{\lambda}{\rho c_p} \frac{\partial T}{\partial r} \cdot A \left| \begin{array}{c} m_- \\ m_+ \end{array} \right| + \frac{\dot{Q}_R}{\rho c_p} \left| \begin{array}{c} m_+ \\ m_- \end{array} \right| \tag{A.78}
\]

Applying spatial and temporal discretization for an implicit scheme:

\[
\frac{T_m^{(t+1)} - T_m^{(t)}}{\Delta t} \cdot V_m = -\frac{\lambda}{\rho c_p} \cdot A \left| \begin{array}{c} T_m^{(t+1)} - T_m^{(t)} \\ (\Delta r)_m \\ (\Delta r)_{m+1} \end{array} \right| - \frac{\lambda}{\rho c_p} \cdot A \left| \begin{array}{c} T_m^{(t+1)} - T_m^{(t)} \\ (\Delta r)_{m-1} \end{array} \right| + \frac{\dot{Q}_R}{\rho c_p} \left| \begin{array}{c} m_+ \\ m_- \end{array} \right| \tag{A.79}
\]

Applying this discretization to all cells results in a system of linear equations, which can be written as

\[
M \tilde{T} = \tilde{b} \tag{A.80}
\]

where \( M \) is a sparse \((m \times m)\) matrix with the transport coefficients, \( \tilde{T} \) the solution vector containing the temperatures \( T_m^{t+1} \) and \( \tilde{b} \) the load vector. The equation system can be solved by a tridiagonal matrix algorithm to attain the
values of \( \bar{T} \). The entries of \( M \) and \( \vec{b} \) are found by rearranging eq. A.79:

\[
M_{m,m-1} = -\frac{\Delta t}{V_m} \cdot \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{m-}
\]

(A.81)

\[
M_{m,m} = 1 + \frac{\Delta t}{V_m} \left( \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{m-} + \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{m+} \right)
\]

(A.82)

\[
M_{m,m+1} = -\frac{\Delta t}{V_m} \cdot \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{m+}
\]

(A.83)

\[
b_m = \frac{\Delta t}{V_m} \cdot \frac{\dot{Q}_R}{\rho c_p} \bigg|_{m} + T_m(t)
\]

(A.84)

**Boundary cells** At the inner boundary \((m = 1)\), there is no inward or bottom neighbor cell. For the long cylinder (discretization in radial direction), a symmetry boundary condition is applied, with no heat transfer over the inner boundary. The corresponding transport matrix entries and the load vector are then:

\[
M_{1,1} = 1 + \frac{\Delta t}{V_1} \cdot \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{1+}
\]

(A.85)

\[
M_{1,2} = -\frac{\Delta t}{V_1} \cdot \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{1+}
\]

(A.86)

\[
b_1 = \frac{\Delta t}{V_1} \cdot \frac{\dot{Q}_R}{\rho c_p} \bigg|_{1} + T_1(t)
\]

(A.87)

For the flat cylinder, the boundary condition is given by a contacting wall. Using the approximation that the interface temperature is the same as the temperature in the cell center \((T_{1-} \approx T_1)\), the entries for \( M \) and \( \vec{b} \) are found from:

\[
M_{1,1} = 1 + \frac{\Delta t}{V_1} \left( \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{1+} + \frac{\lambda_c A_c}{\rho c_p s_c} \right)
\]

(A.88)

\[
M_{1,2} = -\frac{\Delta t}{V_1} \cdot \frac{\lambda A}{\rho c_p (\Delta r)} \bigg|_{1+}
\]

(A.89)

\[
b_1 = \frac{\Delta t}{V_1} \cdot \left( \frac{\dot{Q}_R}{\rho c_p} \bigg|_{1} + T_1(t) + \frac{\lambda_c A_c}{\rho c_p s_c} T_c \right)
\]

(A.90)

In the above equations, the index \( c \) refers to the contact structure, where \( \lambda_c \) is the thermal conductivity, \( s_c \) the wall thickness and \( T_c \) the outside temper-
nature of the contacting wall.

At the interface towards the bulk gas cell heat transfer occurs by convection and radiation. Radiation is included as a source term, whereas the convective heat transfer is included in matrix $M$:

$$M_{m,m-1} = -\frac{\Delta t}{V_m} \cdot \frac{\lambda A}{\rho c_p (\Delta r)}_{m-} \quad (A.91)$$

$$M_{m,m} = 1 + \frac{\Delta t}{V_m} \cdot \left( \frac{\lambda A}{\rho c_p (\Delta r)}_{m-} + \frac{\alpha_s A_s}{\rho c_p} \right) \quad (A.92)$$

$$M_{m,m+1} = -\frac{\Delta t}{V_m} \cdot \frac{\alpha_s A_s}{\rho c_p} \quad (A.93)$$

$$b_m = \frac{\Delta t}{V_m} \cdot \left( \frac{\dot{Q}_R}{\rho c_p} \right)_{m} + \frac{\dot{Q}_{s-w} \cdot A_s}{\rho c_p} \right) + T_m^{(t)} \quad (A.94)$$

**Bulk gas cell** The enthalpy balance (eq. A.26) in the bulk gas is integrated as:

$$\frac{\partial (\rho T)}{\partial t} c_p V_m = \dot{H}_{in} - \dot{H}_{out} + \dot{H}_{s-g} - \alpha_s A_s (T_m - T_{m-1}) - \alpha_w A_w (T_m - T_w) \quad (A.95)$$

Applying the discretization scheme:

$$\frac{(\rho c_p T)^{(t+1)}_m - (\rho c_p T)^{(t)}_m}{\Delta t} \cdot V_m = \dot{H}_{in} - \dot{H}_{out} + \dot{H}_{s-g} - \alpha_s A_s (T_m^{(t+1)} - T_{m-1}^{(t+1)}) \quad (A.96)$$

$$- \alpha_w A_w (T_m^{(t+1)} - T_w)$$

In the above, the heat transfer coefficients $\alpha$ and areas $A$ are indexed $s$ and $w$, referring to the wall and solid side boundaries, respectively. The temperature $T_{m-1}^{(t+1)}$ is that of the neighboring solid cell (see above). The term $\dot{H}_{s-g}$ is the enthalpy carried by the gas stream emitted from the bulk solid. The
coefficients of transport matrix and load vector are then:

\[ M_{m,m-1} = -\frac{\Delta t}{V_m} \cdot \frac{\alpha_s A_s}{(\rho c_p)^{(t+1)}} \]  
(A.97)

\[ M_{m,m} = 1 + \frac{\Delta t}{V_m} \cdot \frac{\alpha_s A_s + \alpha_w A_w}{(\rho c_p)^{(t+1)}} \]  
(A.98)

\[ b_m = \frac{\Delta t}{V_m} \cdot \frac{\dot{H}_{in} - \dot{H}_{out} + \dot{H}_{s-g} + \alpha_w A_w T_w + (\rho c_p T)^{(t)}}{(\rho c_p)^{(t+1)}} \]  
(A.99)

### A.5.1.3. Gaseous species balance

**Internal cells** Integrating over volume and surfaces in equation A.23 with substitutions (eq. A.33) yields:

\[ \frac{\partial C_i}{\partial t} \cdot V_m = -D \frac{\partial C_i}{\partial r} \cdot A \bigg|_{m=} -D \frac{\partial C_i}{\partial r} \cdot A \bigg|_{m=} \]

\[ -C_i R \frac{\kappa}{\eta} \frac{\partial (C_i T / y_i)}{\partial r} \cdot A \bigg|_{m=} -C_i R \frac{\kappa}{\eta} \frac{\partial (C_i T / y_i)}{\partial r} \cdot A \bigg|_{m=} \]

\[ + \dot{n}_{i,R} \bigg|_m \]  
(A.100)
The above equation is discretized in time and space for each species \( i \) by the following expression:

\[
\frac{C_{i,m}^{(t+1)} - C_{i,m}^{(t)}}{\Delta t} \cdot V_m = -D \cdot A_{m-} \frac{C_{i,m}^{(t+1)} - C_{i,m-1}^{(t+1)}}{(\Delta r)_{m-}} - D \cdot A_{m+} \frac{C_{i,m}^{(t+1)} - C_{i,m+1}^{(t+1)}}{(\Delta r)_{m+}}
\]

\[
-C_i R \frac{K}{\eta} \cdot A_{m-} \frac{(C_i T/y_i)_{m}^{(t+1)} - (C_i T/y_i)_{m-1}^{(t+1)}}{(\Delta r)_{m-}} - C_i R \frac{K}{\eta} \cdot A_{m+} \frac{(C_i T/y_i)_{m}^{(t+1)} - (C_i T/y_i)_{m+1}^{(t+1)}}{(\Delta r)_{m+}} + \dot{n}_{i,R}|_m
\]

(A.101)

This yields a linear system of equations, which can be written in matrix form and solved by a tridiagonal algorithm for each species independently:

\[
M_i \tilde{C}_i = \tilde{b}_i
\]

(A.102)

Terms \( C_{i|m-} \) and \( C_{i|m+} \), i.e. the concentrations at the cell interfaces, appear in the advective terms. Their values are determined by an upwind scheme, where

\[
C_{i|m-} = \begin{cases}
C_{i,m}, & \frac{(C_i T/y_i)_{m}^{(t+1)} - (C_i T/y_i)_{m-1}^{(t+1)}}{(\Delta r)_{m-}} > 0 \\
C_{i,m-1}, & \frac{(C_i T/y_i)_{m}^{(t+1)} - (C_i T/y_i)_{m-1}^{(t+1)}}{(\Delta r)_{m-}} < 0
\end{cases}
\]

(A.103)

\[
C_{i|m+} = \begin{cases}
C_{i,m}, & \frac{(C_i T/y_i)_{m}^{(t+1)} - (C_i T/y_i)_{m+1}^{(t+1)}}{(\Delta r)_{m+}} > 0 \\
C_{i,m+1}, & \frac{(C_i T/y_i)_{m}^{(t+1)} - (C_i T/y_i)_{m+1}^{(t+1)}}{(\Delta r)_{m+}} < 0
\end{cases}
\]

(A.104)

The value of cell \( m \) is used if the flow is outward, and that of the neighboring cell \((m - 1 \) or \( m + 1 \)) if the flow is inward. Unlike averaging or linear interpolation of the interface value using the adjacent cells, this scheme is numerically stable (see e.g. [207]).

The coefficients of the transport matrices \( M_i \) and load vectors \( \tilde{b}_i \) are calcu-
lated by rearranging eq. A.101:

\[
M_{m,m-1} = -\frac{\Delta t}{V_m} \left( D_{m-} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{m-} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{m-} \quad \text{(A.105)}
\]

\[
M_{m,m} = 1 + \frac{\Delta t}{V_m} \left( D_{m-} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{m} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{m-} + \left( D_{m+} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{m+} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{m+} \quad \text{(A.106)}
\]

\[
M_{m,m+1} = -\frac{\Delta t}{V_m} \left( D_{m+} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{m+} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{m+} \quad \text{(A.107)}
\]

\[
b_m = \frac{\Delta t}{V_m} \cdot \tilde{n}_{i,R|m} + C_{i,m}^{(t)} \quad \text{(A.108)}
\]

**Inner boundary cell** The inner boundary is either impermeable or a symmetry boundary condition is applied. In both cases, the inner flux is zero. The corresponding coefficients of \( M_i \) and \( \tilde{b}_i \) are:

\[
M_{1,1} = 1 + \frac{\Delta t}{V_1} \left( D_{1+} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{1+} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{1+} \quad \text{(A.109)}
\]

\[
M_{1,2} = -\frac{\Delta t}{V_1} \left( D_{1+} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{1+} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{1+} \quad \text{(A.110)}
\]

\[
b_1 = \frac{\Delta t}{V_1} \cdot \tilde{n}_{i,R|1} + C_{i,1}^{(t)} \quad \text{(A.111)}
\]

**Bulk gas cell** The bulk gas cell has no outward neighbor, so that the corresponding diffusion and advective terms disappear. Transport of species into and out of the domain is included in the load vector \( \tilde{b}_1 \). No reactions are modelled in the bulk gas phase.

\[
M_{m,m-1} = -\frac{\Delta t}{V_m} \left( D_{m-} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{m-} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{m-} \quad \text{(A.112)}
\]

\[
M_{m,m} = 1 + \frac{\Delta t}{V_m} \left( D_{m-} + C_i R \frac{K}{\eta} \left| \frac{T}{y_i} \right|_{m} \right) \cdot \frac{A}{(\Delta r)} \bigg|_{m} \quad \text{(A.113)}
\]

\[
b_m = \frac{\Delta t}{V_m} \cdot (\dot{n}_{i,\text{in}} - \dot{n}_{i,\text{out}}) + C_{i,m}^{(t)} \quad \text{(A.114)}
\]
A.6. Additional modelling results

Results from simulating CO and CO$_2$ are summarized in Figures A.42 to A.44. The stoichiometric coefficients used can be calculated from Table 6.3. Corresponding temperature profiles of the experiments in 20% oxygen atmosphere are found in Figure 6.5. Experimental data (symbols) are the same in Figures A.43 and A.44 (oxidation models I and II, respectively).
Figure A.42.: Pyrolysis model
Figure A.43.: Oxidation model I
Figure A.44.: Oxidation model II