1. Introduction

1.1 Motivation

Climate change represents one of the greatest challenges of the 21st century, with its consequences affecting the entire global population. The primary driver of climate change are anthropogenic CO_2 emissions, which originate predominantly from emission-intensive sectors, such as power generation, heat production and the transportation sector. According to [1], coal combustion alone accounts for approximately one third of the anthropogenic CO_2 emissions. Technical solutions such as solar and wind power are proposed in the energy sector to reduce CO_2 emissions associated with power consumption. As these mentioned techniques are characterized by significant temporal fluctuations in electricity generation, the importance of alternative, reliable and clean energy provision becomes evident. Despite the growing interest in renewable alternatives, combustion processes remain a fundamental pillar of energy systems, providing essential services for baseline energy demand and infrastructure stability. Alternatively, storing energy from renewable sources is required to ensure a stable energy supply without temporal fluctuations. Energy storage can be achieved through various methods, including electrical, electrochemical, mechanical, thermal, or chemical storage. Each storage technology differs in terms of discharge duration and storage capacity, influencing its suitability for specific applications. [2]

In addition to energy storage, carbon capture technologies represent another approach to reduce CO_2 emissions. Carbon capture technologies are conventionally divided into three principal approaches, which include pre-combustion capture, oxy-fuel combustion and post-combustion capture. Among these, oxy-fuel combustion is particularly attractive for energy generation, as pulverized fuel boilers can be retrofitted more efficiently compared to other technologies. Furthermore, oxy-fuel combustion allows for the utilization of a wide range of pulverized fuels, including biomass and coal, highlighting its versatility and broad applicability. [3]

In oxy-fuel combustion, pulverized fuels are burned in an atmosphere consisting of oxygen, carbon dioxide and water vapor. Typically, CO_2 originates from recirculated flue gas, which is mixed with pure oxygen to regulate combustion conditions. After the combustion process, CO_2 separation is achieved by condensing water vapor from the flue gas stream. When the captured CO_2 is subsequently stored, the process is classified as carbon capture and storage (CCS). This enables the combustion of pulverized fuels, such as high volatile bituminous coal and lignite, while minimizing or neutralizing associated carbon emissions. [3,4]

When this process is applied to biogenic solid fuels, negative carbon dioxide emissions are achievable. Through photosynthesis, biomass absorbs atmospheric CO_2 and if the released CO_2 during combustion is captured and permanently stored, the overall carbon balance becomes negative. This approach is referred to as biomass in combination with carbon capture and storage (BECCS) [5], providing a potential pathway for active CO_2 removal from the atmosphere.

For both the retrofitting of existing power plants as well as the design and construction of new facilities, a fundamental understanding of solid fuel combustion in oxy-fuel atmospheres is essential. Although coal-fired power plants are being phased out in Germany by 2038 [6] and indirectly by 2050 through the European green deal for the whole of Europe [7], the global energy sector requires ongoing research into the fundamental mechanisms of coal combustion in oxy-fuel environments.This knowledge is crucial for enabling other countries and regions to consider transitioning to oxy-fuel combustion technologies. Moreover, further investigation into biomass combustion in oxy-fuel atmospheres is imperative to unlock the potential for achieving negative CO_2 emissions on a broader scale.

1.2 Key scientific questions researched in this work

The combustion of solid fuels is a complex process influenced by multiple interacting parameters. The relevance of various influencing factors and the understanding of the combustion of solid fuels are essential for their application in emerging scientific fields, such as the utilization of alternative renewable fuels (e.g. Metal Fuels as an alternative fuel in a recyclable cycle) and novel combustion technologies (e.g. oxy-fuel, co-firing). To accurately characterize and validate simulations of novel or established combustion systems or single-particle simulations, high-quality experimental data is essential. A combination of invasive and non-invasive measurement techniques is required to obtain comprehensive and detailed datasets for comparison with simulations. Furthermore, to investigate specific combustion characteristics like char particle temperature or particle composition throughout the burnout, all other influencing parameters must be maintained under constant conditions.

The primary aim of this work is to generate a comprehensive dataset on single-particle and group combustion of various fuel particles to support the validation of novel simulation models. Furthermore, all relevant influencing parameters regarding the transition from single particle to group particle combustion will be examined, discussed and potential reasons for the particularities between both combustion modes systematically provided. Building on these findings, the applicability of the measurement techniques will be assessed for other research areas, such as fire suppression, and for less common renewable fuel particles.

The first subject area defines the fundamental principles of this work with the publication titled “Combustion of single walnut shell particles in a laminar flow reactor under oxy-fuel conditions: Optical measurements and particle sampling”. In this work, the primary objective is to generate a new dataset on the single-particle combustion of walnut shells. Walnut shells are representative of lignocellulosic, lignin-rich biomass and are widely considered a renewable energy source. In the literature, walnut shell particles have been investigated not only in single-particle experiments [8–10] but also in semi-industrial scale combustion processes [11–13], in studies addressing the overall combustion process [14–16], and as part of various numerical simulations [17,18]. Their broad relevance across experimental and computational research underlines the importance of further detailed investigations. The newly developed dataset provides a high level of detail, a critical requirement for validating single particle combustion models. The optical measurements and those obtained using the sampling probe represent the most comprehensive dataset within the available literature regarding eight different oxy-fuel atmospheres to date. Additionally, the publication includes a comprehensive review of the current state of research on oxy-fuel combustion of biomass, where all significant studies have been systematically compiled in a table.

The second subject area focuses on the transition from single particle combustion to group particle combustion with the title “Particle temperature and composition measurements in the ignition phase of single coal particles and particle groups under conventional and oxy-fuel atmospheres”. Building on earlier numerical and experimental studies on the transition from single-particle to group combustion, this work employs the same fuel particles and the same burner as in the previous publications to ensure comparability. Key aspects include the identification and analysis of characteristic parameters that define group particle combustion, as well as the measured and identified differences between single and group particle combustion. Furthermore, comparative analysis is investigated between oxy-fuel and air-based atmospheres to assess how combustion characteristics evolve as the transition from single particle to group particle combustion takes place.

The third subject area of this thesis is the transfer of the first two subject areas and the publication is titled “Optical measurements of emissivity, flame and char temperatures of pulverized pine needles in a drop tube furnace”. This study employs the same optical measurement techniques as the first two research areas but utilizes different cameras and a distinct reactor setup. The reactor used in this investigation is a drop tube furnace with experiments done under an air-based atmosphere. A novel biomass, not previously considered as a pulverized fuel, is examined for its potential use in power plants. Thus, various grinding settings were analyzed to achieve the necessary particle size. Furthermore, the study aims to give first insights of the findings to fire prevention and suppression research, providing measuring data of typical combustion factors (e.g. temperature, emissivity) of pine needle fires.

2. Fundamentals of pulverized solid fuel combustion

2.1 Solid carbonaceous fuels

Solid fuels can be classified according to their degrees of carbonization. Carbonization describes the natural transformation of buried plant material into a dense, dry, carbon-rich and hard substance. This process is primarily driven by heat and pressure over a period of millions of years. The duration of carbonization divides the solid fuels into the following types: anthracite, bituminous coal, sub-bituminous coal and lignite. Peat can also be classified as a fossil fuel. In contrast, biomass refers to organic material derived from living or recently living organisms and is categorized as a renewable fuel. The various types of solid carbonaceous fuels differ in terms of their higher heating value (HHV), ash content, volatile components, moisture content and elemental composition. [19,20]

The van Krevelen diagram represents a fundamental graphical instrument for the characterization and classification of solid carbonaceous fuels. An example of such a diagram is shown in Figure 1. In the van Krevelen diagram, the atomic hydrogen-to-carbon (H/C) ratio is plotted on the ordinate, while the atomic oxygen-to-carbon (O/C) ratio is plotted on the abscissa.

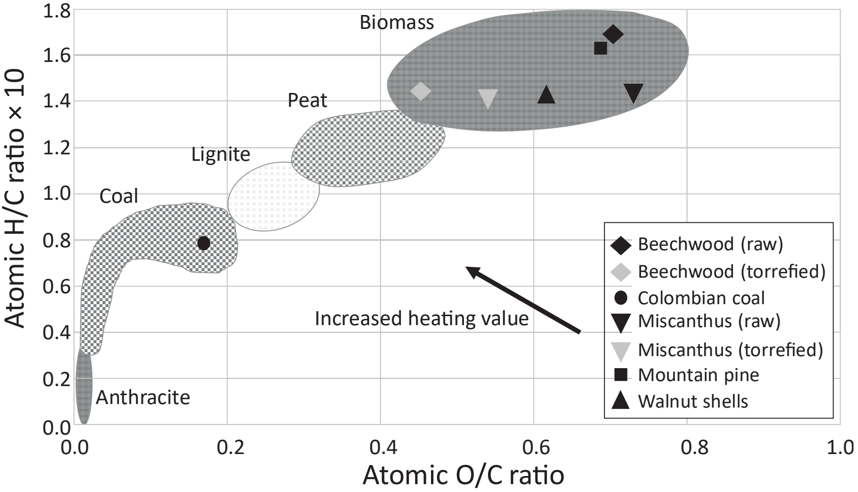

Figure 1: Van Krevelen diagram including typical solid carbonaceous fuels investigated in this work (modified from [21]).

Fuels with the highest level of carbonization exhibit the lowest atomic oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios. Consequently, anthracite is located near the origin in the van Krevelen diagram. As the level of carbonization decreases, the O/C and H/C ratios increase. Accordingly, bituminous coal, lignite, peat and biomass align along the diagram's first angle bisector in the first quadrant in ascending order. The heating value increases as the atomic oxygen-to-carbon ratio decreases and the hydrogen-to-carbon ratio increases. One method to upgrade the renewable fuel biomass is the process of torrefaction. Torrefaction is a thermal process with temperatures up to 300 °C in the absence of oxygen. During this process, shorter-chain C-H compounds are released and the high heating value of the biomass is increased. Torrefied biomass is in proximity to peat within the van Krevelen diagram. The arrow in the figure indicates the direction of increasing heating value. The heating value rises with an increasing H/C ratio and a decreasing O/C ratio. [22,23]

2.1.1 Coal

Coal is classified as a fossil energy carrier. Its chemical composition and crystalline structure are highly complex and not easily described. Fundamentally, coal is categorized into fractions such as moisture, volatile matter, fixed carbon and ash. These individual components can be determined through various analytical methods. These methods include drying, heating in the absence of air/oxygen and ashing. The specific methods for determining the respective fractions are documented in the following DIN standards [24–26]. [19]

The classification of coal into bituminous coal or lignite is based on its calorific value and its carbon content according to [27]. According to DIN [27], coal with a calorific value exceeding 24 MJ/kg is characterized as bituminous coal, while values below this threshold and a carbon content between 55 % and 75 % classify it as lignite. Furthermore, the categorization of various bituminous coals is carried out according to their volatile matter content, as specified in the DIN standard. In addition to the classification according to DIN standards, there are other coal classification systems, such as ASTM (American Society for Testing and Materials) and GB (Guobiao).

Beyond the classification of coal, the amount of volatile matter content plays a crucial role in the combustion process. The volatiles together with the fixed carbon are the combustible part of the particle. This combustible fraction is composed of carbon, hydrocarbons and oxygen. During pyrolysis, the volatile matter is released from the coal in the absence of oxygen and the residue consists of ash and fixed carbon. The fixed carbon is consumed during the solid-phase combustion following pyrolysis. At the end of the combustion process, the particle consists of the non-combustible ash fraction. The mineral content of the ash primarily comprises metal oxides, including those of Al, Si, Fe, Ca, Mg, K and Na. Beyond mineral components, the ash also incorporates fractions of the fuel sulfur in the form of SO_3 compounds. [28]

2.1.2 Biomass

Primary biomass, derived from organic matter of living organisms, is produced through photosynthesis, where solar energy is converted into chemical energy stored in plant materials. In contrast to biomass, which originates from recently living organisms, coal is formed through the geological transformation of dead organic matter over millions of years. Biomass primarily includes lignocellulosic resources, such as agricultural and forestry residues, serving as a renewable energy source, which are not used for food or feed. [28,29]

Biomass predominantly consists of three main elements of carbon, hydrogen and oxygen. In addition to the three main elements, marginal amounts of nitrogen, sulphur and ash are also present. In Table 1 the different biomass fuels, which are used in this work, are compared to coal, a typical high volatile bituminous coal, which is also part of this thesis. The biomass samples were torrefied at a temperature of 275 °C with a residence time of 30 minutes. In addition, Table 1 shows the proximate, ultimate analysis, high heating value and the particle sizes of the relevant fuels for this study, which are all part of this thesis. [29,30]

Table 1: Analysis of various biomass fuels and a typical hvb coal for comparison reasons, concentrations in [%$_m$]

Fuel	Fraction [µm]	ash$_d$	volatiles$_d$	C$_{daf}$	H$_{daf}$	N$_{daf}$	S$_{daf}$	O$_{daf}$	HHV$_{daf}$ [MJ/kg]
hvb	106 – 125	4.80	40.09	79.00	5.39	1.78	0.88	13.0	32.48
WS	125 - 150	0.41	80.79	52.27	5.82	0.24	0.02	41.65	20.514
PN	200 - 315	3.42	78.99	49.90	6.42	0.57	0.01	42.11	21.15
BW	106 – 125	0.68	85.43	45.60	4.21	0.21	-	49.98	18.50
TPN	200 - 315	5.81	68.75	51.37	5.76	0.57	0.01	42.30	23.83
TBW	106 – 125	0.95	75.04	53.79	4.98	0.36	-	40.87	21.14

d ≙ dry, daf ≙ dry ash free, hvb ≙ high volatile bituminous coal, WS ≙ walnut shells, PN ≙ pine needles, BW ≙ beech wood, TPN ≙ torrefied pine needles, TBW ≙ torrefied beech wood

Typical biomass is characterized by significantly higher volatile matter content than fossil fuels such as coal. As indicated in Table 1, all raw biomass display volatile matter contents around 80 %$_m$, with the associated torrefied biomass showing a 10 %$_m$ lower value compared to the raw materials. In comparison, a typical high volatile Colombian coal exhibits a volatile matter content of 40 %$_m$. Another notable difference is observed in the ash content, where biomass (e.g. beech wood or walnut shells) contains less than 1 %$_m$ ash, while the example coal contains approx. 5 %$_m$. In terms of elemental composition, biomass typically have a carbon content of around 50 %$_m$ and an oxygen content of 40 – 50 %$_m$, whereas hard coals are characterized by a carbon content of about 80 %$_m$ and an oxygen content of roughly 13 %$_m$.

The three main components of lignocellulosic biomass are cellulose, hemicellulose and lignin building the cell wall of plants. The main components are heterogeneously distributed within the cell wall, fulfilling distinct structural functions as the skeleton, linking matrix and hard solids. The schematic structure of biomass with its three main components is illustrated for a pine needle in Figure 2, showing different size scales.

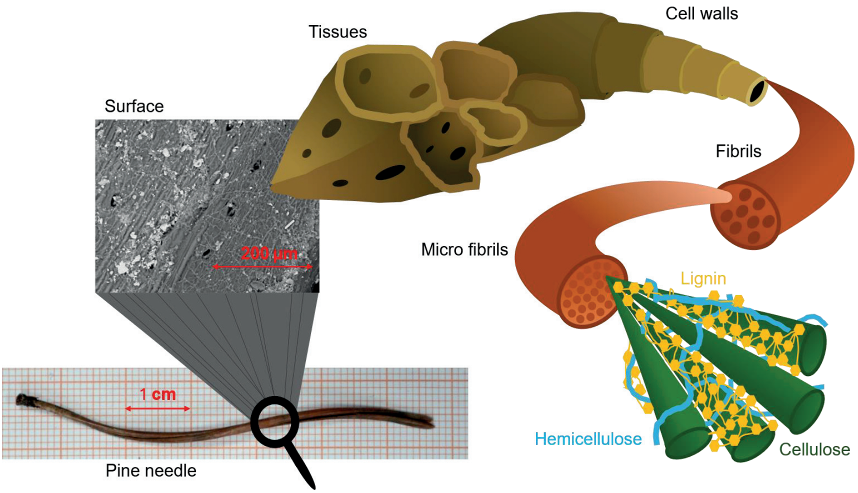

Figure 2: Multi-scale overview of exemplary biomass hierarchical structure, ranging from the entire pine needle (left) to the tissues, individual cells or fibres and the molecular level of cellulose, hemicellulose, and lignin (bottom right) (inspired by [29,31]).

Cellulose molecules form tough microfibrils that serve as the skeleton material of the plant cell wall. The interstitial spaces are filled with amorphous hemicellulose and hard lignin, which function as linking and reinforcing components. The interaction between cellulose and hemicellulose or lignin is primarily governed by hydrogen bonding, whereas the association between hemicellulose and lignin involves both hydrogen and covalent bonds. Furthermore, biomass also contains free components like extractives. The extractives are characterized by non-structural compounds including typically fat, resin, pigment, starch and paraffin. The composition and the content of cellulose, hemicellulose, lignin and the extractives play a role regarding the physical and chemical behaviour of biomass and also directly impact the combustion behaviour of biomass. [29,32,33]

Cellulose accounts for over 50 $\%_m$ of the carbon present in lignocellulosic biomass. As depicted in Figure 2, cellulose is structurally enclosed by hemicellulose and lignin, making selective extraction of individual constituents particularly challenging. Hemicellulose is distributed across multiple layers of the plant cell wall and exhibits a chain-like structure similar to cellulose, characterized with a lower polymerization degree. This results in slightly increased reactivity for hemicellulose compared to cellulose, primarily due to its amorphous structure. As a result, hemicellulose becomes difficult to extract in pure form, thus representative model compounds such as xylan, mannan and galactose are typically used in experimental studies [34]. Lignin is a structural filler and bonding material, contributing to the mechanical stability of biomass and enhancing its resistance to microbial degradation. It is composed of amorphous, thermoplastic polymers that are fragile at room temperature and characterized by a melting point and a glass transition temperature. Below the glass transition temperature, lignin exists in a rigid, glassy state, whereas above it, the material softens and becomes cohesive. The softening temperature decreases significantly with increasing moisture content, as water operates as a plasticizer. [29]

2.2 Combustion

Combustion is one of the fundamental processes for energy supply and also plays a significant role in industrial applications and heating systems. The aim of the combustion process is to convert the chemically bound energy in the fuel through oxidation and transform it into useable heat. Fuel types for combustion are divided into solid fuels (e.g. coal, biomass), liquid fuels (e.g. diesel, ethanol) and gaseous fuels (e.g. natural gas, syngas). In the scope of this thesis, the focus is on solid fuel combustion. The thesis investigates the combustion behaviour of solid fuels, including their thermochemical conversion and influencing parameters.

2.2.1 Combustion of solid fuels

The combustion of solid fuels can be carried out using various combustion systems, according to [19,28,35]. The combustion systems are divided into grate firing, fluidized bed, circulating fluidized bed and pulverized fuel firing. In this order, the gas velocity progressively increases. The focus of this work is the investigation of single particle and the transition to group combustion in a pulverized fuel system. Therefore, the relevant literature on the other combustion systems is referenced to [19,35] for further details.

The combustion process of solid fuels is divided into the main phases of drying, pyrolysis, ignition and combustion. The schematic procedure of the combustion of solid fuel particles is illustrated in Figure 3. The thermal decomposition of the solid fuel at the beginning of the process is initiated by heating. The particles heat up primarily due convection and radiation. The solid fuel particle ignites when it reaches an apparent ignition temperature under the given ambient conditions and when a minimum amount of the released volatile matter combusts rapidly enough to accelerate the overall process. Without sufficient volatile combustion, stable ignition does not occur. Once established, ignition marks the onset of the combustion process, which proceeds through homogeneous and heterogeneous reaction stages. Depending on various factors (e.g. fuel type, fuel composition, firing type etc.) these two reaction types can overlap or proceed sequentially.

In the following, the various stages of the combustion process are examined in greater detail. Commencing with the drying process, this step initiates at 100 °C (approx. 370 K). At this temperature, water evaporates, starting from the surface of the particles and continuing within the particles through the pores. As the temperature rises to 300 °C (approx. 570 K), water is evaporated and released from the fuel. [36]

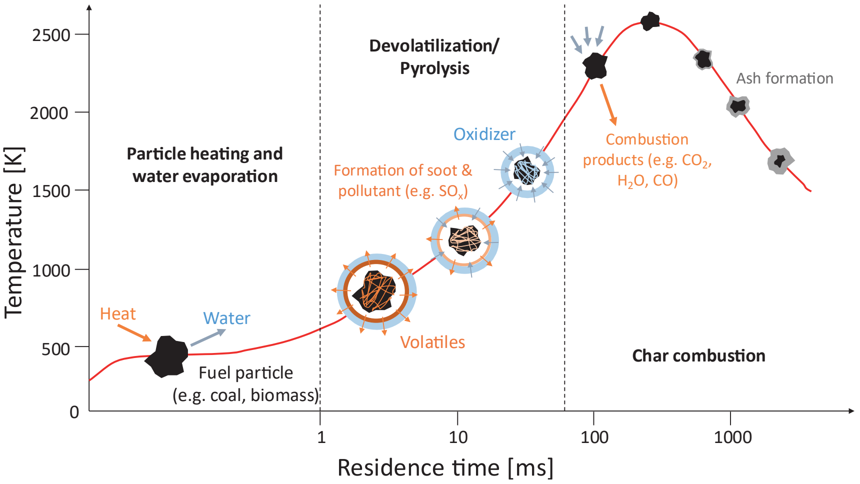

Figure 3: Schematic sequence of the combustion of solid fuel particles (inspired by [36,37]).

The second step is pyrolysis or devolatilization. A distinction is made between fast and slow pyrolysis. Fast pyrolysis is termed as flash pyrolysis (t_{res} ~ <0.5s), while slow pyrolysis (t_{res} ~ minutes/hours) includes processes such as torrefaction. The primary characteristic of this phase is the thermal decomposition of macromolecular structures within the particle during continued heat treatment. During this process, various liquid (e.g. tar), gaseous (e.g. low boiling hydrocarbons) and solid products (e.g. char) are formed. The release of these volatiles (tars and gas) from the particle leads to absence of external oxygen in the vicinity of the particle. The yield distribution of the three product groups resulting from pyrolysis is dependent on factors such as temperature, residence time, operational conditions within the reactor and the investigated solid fuel. [30,38]

The combustion process starts with the ignition. The ignition temperature is defined as the minimum temperature at which a fuel will ignite and sustain combustion without an external source. Below this temperature, the heat generated during fuel oxidation is lost to the environment, preventing a significant rise in temperature. It is only at or above the ignition temperature that the reaction rate increases to a point where the heat produced surpasses the heat dissipated to the surroundings. There are two individual ignition points in the combustion of solid fuels divided into volatile components and residual char. Volatile components ignite when they form a combustible mixture with oxygen-containing gas and reach 500 - 700 °C (approx. 770 - 970 K). Residual char ignites above 800 °C (approx. 1070 K) when sufficient oxygen is present at its surface. The main parameters influencing ignition are the heating rate, particle size, composition of the solid fuel and the oxygen content in the atmosphere. Fundamentally, three ignition mechanisms are distinguished. In the first mechanism, volatile matter burns in a gas atmosphere surrounding the particle. In the second mechanism, there is simultaneous ignition of volatile matter around the particle and residual char. The third mechanism, characteristic of