Chapter 1

Introduction

The last centuries were marked by a large-scale industrial development due to the use of fossil fuels which are the main source of energy not only for heating but also for power generation and transportation. As a consequence of this increased consumption of fossil fuels, two major features have to be taken into account. First, fossil fuels are not renewable, thus leading to a deficit of fuels when their sources will be depleted. Furthermore, the burning of fossil fuels by humans is the largest source of emissions of carbon dioxide, which is one of the greenhouse gases that contributes to the global warming of the Earth. Other emissions during combustion processes are soot, often thought to be cancerogeneous, and NO_x, responsible for the acid rain and the ozon formation.

That is the reason of the necessity to increase the efficiency of the combustion and reduce pollutant formation. Then for example, more power could be obtained by consuming less fuel and emitting no or less pollutant.

It implies a good understanding of all the processes taking place during the combustion. For that purpose, the models of these complex processes are still subject to intensive research.

Until 2020 it is foreseen to build many new power plants in Germany and Europe due to the aging of those currently in use. Furthermore an increase of the power installations in Europe is already predicted [35].

It is not clear whether the renewable energies will be able to cover this need. Since the future contributions from the nuclear energy cannot be predicted, there remains the use of fossil fuels. Because of the disponibility, delivery guarantee and economics on a long-time scale, the use of coal is particularly

interesting.

Nevertheless, an increasing use of coal also results in an increase of CO_2 emission, which is in contradiction to the 1997 Kyoto protocol [86] ratified by 168 nations and one regional economic integration organization (the EEC) as of the 26 February 2007. Of these, 35 countries and the EEC are required to reduce greenhouse gas emissions below levels specified for each of them in the treaty. These add up to a total cut in greenhouse-gas emissions of at least 5% from 1990 levels in the commitment period 2008-2012.

In order to overcome this problem, new techniques are developed. One of them consists in a combustion not with combustion air for the oxidizer as usually done, but with a mixture of oxygen and flue gas, the oxygen being supplied by a high temperature membrane. It is the OXYCOAL-AC process [61].

Nowadays the development of such new techniques is supported by three-dimensional simulations which have the advantage of giving an insight into the combustion processes on a short-time scale with low costs compared to what experiments would offer. For that purpose, the models used in the Computational Fluid Dynamics (CFD) for the combustion processes must be reliable to give results of good quality. Many studies were already done in the past for different regimes and under different configurations (for example Diesel combustion [6], MILD combustion [18], [37], premixed [32] and partially premixed combustion [19]) with different fuels such as methane [8], [7], [54], [10], [80], n-heptane [20], [12], n-decane [23], [13] as well as multi-component fuels [73].

For the coal combustion as well as for gaseous combustion such as in industrial furnaces, special attention on the reaction mechanisms should be paid. Combustion takes place in reaction chains. Chemical kinetic reaction mechanisms describe all the chemical processes during the combustion from fuel oxidation to pollutant formation. A chemical kinetic mechanism is thus the basis for a good simulation. The field of kinetics has been the object of scientific studies for a long time. However there still is a need to improve the existing data, especially under certain boundary conditions that were not used until now. Once validated against various experimental data, these detailed reaction mechanisms are introduced into complex multi-dimensional fluid dynamics codes for combustion simulations. Despite the increasing computational capacities, those detailed mechanisms may be too long for CFD simulations and then require too much calculation time. The reduction of reaction mechanisms is particularly attractive since it enables to reduce the

computational effort without losing much information.

A major objective of this work has been to develop and upgrade kinetic mechanisms for model fuels in order to simulate the complex physico-chemical interactions in pratical combustion systems. The mechanisms, after they have been assembled, have been validated against a wide range of combustion regimes.

In chapter 2 the mathematical models for simulating the combustion are presented. Then the laminar flamelets are introduced and the RIF concept is described.

In chapter 3 a model to calculate three-dimensional combustion processes is explained. It is based on the flamelet model, which considers the chemical reaction kinetics isolated from the flow dynamics. This is made possible thanks to the assumption of the existence of very thin layers in which the chemical processes occur. These laminar thin layers in the turbulent flow are called flamelets. The flamelet model enables the calculation of ignition, heat release and pollutant formation under consideration of detailed and reduced chemical reaction kinetics. The consideration of combustion as an unsteady process is of particular interest. This is achieved by using unsteady flamelets. The flamelets are interactively calculated with a flow solver for a particular path of particles through the furnace. That is why these flamelets are called Representative Interactive Flamelets. The statistical path of a fluid particle through the furnace is described by the Eulerian transport equations.

The developed chemical mechanism for the description of the detailed reaction kinetics of methane is presented in chapter 4. The detailed mechanism for methane is composed of 143 elementary reactions with 35 species. Further to the reactions to describe the fuel decomposition, the mechanism also contains a detailed description of NO_x formation. This carefully validated mechanism was reduced by introduction of steady-state assumptions.

In chapter 4, the pyrolysis models used for the simulation of the coal combustion in chapter 5 are also described.

To validate the presented models and show the ability of a reduced mechanism to reproduce the results of a detailed numerical simulation of a $FLOX^{\circledR}$ furnace is performed. Flameless oxidation ($FLOX^{\circledR}$) or flameless combustion is a well-known low-NO_x combustion technique for industrial furnaces. The FLOX concept was developed and patented in 1990 by WS [92]. Flameless combustion is based on the principle of internal flue gas recirculation in a combustor. If recirculation rates are high enough and flue gas, combustion

air and fuel are mixed prior to ignition, a diluted homogeneous volumetric combustion mode at a reduced partial pressure of oxygen is established. Distinct flame fronts, as they are typical for lean premixed flames, are replaced by a volume-type flame mode. This combustion mode is characterised by low NO_x emissions because local temperature peaks are avoided [21], [22]. Such a combustor is numerically investigated.

Finally these models were also implemented so as to simulate the coal combustion in a pressurised pulverized coal combustion facility. Special attention was paid to the gaseous phase. The results of the simulations are compared to experimental measurements for both cases.

Chapter 2

Mathematical Models

In this chapter the mathematical models used in the numerical calculations will be presented.

2.1 Conservation Equations

The flow field is described by a system of coupled, non-linear partial differential equations for mass, momentum and energy. In the case of reactive flows these are the so-called Navier-Stockes equations, the conservation equations for the chemical species as well as for the energy. For non-constant density flows the Navier-Stockes equations are formulated in the conservative form as follows:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{2.1}$$

for the continuity and for the momentum as:

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \cdot \tau + \rho \mathbf{g}. \tag{2.2}$$

In Eqs. (2.1) and (2.2) ρ denotes the density, $\mathbf{v}$ the velocity vector and p the pressure. The Newton viscous stress tensor τ is defined by

$$\tau = \left[2\mu \mathbf{S} - (\frac{2}{3}\mu - \kappa)\nabla \cdot \mathbf{v}\mathbf{E} \right], \tag{2.3}$$

where $\mathbf{E}$ is the identity matrix and

$$\mathbf{S} = \frac{1}{2}[\nabla \mathbf{v} + (\mathbf{v})^{T}]. \tag{2.4}$$

Here μ denotes the dynamic viscosity which is related to the kinematic viscosity by

$$\mu = \rho\nu. \tag{2.5}$$

The bulk viscosity κ is small compared to the dynamic viscosity and is therefore usually neglected. The term $\rho\mathbf{g}$ in Eq. (2.2) accounts for buoyancy effects.

Next to the Navier-Stockes equations for continuity and momentum other conservation equations are necessary for the simulation of combustion processes. These are the conservation equations for the chemical species and the energy.
The conservation equation for mass fraction Y_i of chemical species i is given by

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho\mathbf{v}Y_i) = -\nabla \cdot \mathbf{j}_i + \omega_i, \qquad i = 1, 2, ..., n_s, \tag{2.6}$$

where n_s represents the total number of species. $\mathbf{j}_i$ denotes the molecular diffusion flux and ω_i is the chemical source term. The molecular diffusion flux is formally defined as

$$\mathbf{j}_i = \rho(\mathbf{v}_i + \mathbf{v}), \tag{2.7}$$

where $\mathbf{v}_i$ is the mass average velocity of species i. A transport equation for $\mathbf{v}_i$ can be derived (Williams [91]). But the additional effort to solve these equations is not desirable, especially in turbulent flows where the molecular diffusion flux is usually negligible compared to the turbulent transport. Therefore it is useful to consider simplified versions of the diffusive fluxes. Assuming binary diffusion of a species i in another one present in high concentration and according Fick's first law for binary diffusion, the diffusive flux can be described as

$$\mathbf{j}_i = -\rho D_i \nabla Y_i, \tag{2.8}$$

where D_i is the binary diffusion coefficient of species i with respect to an abundant species, for example N_2.

The conservation equation for enthalpy is

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho\mathbf{v}h) = \frac{Dp}{Dt} - \nabla \cdot \mathbf{j}_q + \dot{q}_r. \tag{2.9}$$

In this equation, h is the mass weighted sum of specific enthalpies h_i of species i:

$$h = \sum_{i=1}^{n_s} Y_i h_i. \tag{2.10}$$

The specific enthalpies are calculated with

$$h_i = \Delta h_{f,i}^0 + \int_{T^0}^{T} c_{pi} dT \tag{2.11}$$

as sum of the standard formation enthalpy $\Delta h_{f,i}^0$ taken at the reference temperature T^0 and the thermal enthalpy. The heat flux vector $\mathbf{j}_q$ accounts for thermal diffusion by temperature gradients and enthalpy transport by species diffusion

$$\mathbf{j}_q = -\lambda \nabla T + \sum_{i=1}^{n_s} h_i \mathbf{j}_i, \tag{2.12}$$

where λ is the thermal conductivity. The last term in Eq. (2.9), $\dot{q}_r$, represents radiative heat loss. With the definition of the enthalpy in Eq. (2.10) an alternative formulation for the conservation of energy can be given. With the relation

$$dh = \frac{\partial h}{\partial T} dT + \sum_{i=1}^{n_s} \frac{\partial h}{\partial Y_i} dY_i = c_p dT + \sum_{i=1}^{n_s} h_i dY_i \tag{2.13}$$

this alternative formulation in the form of an energy equation is formulated with temperature:

$$\frac{\partial \rho T}{\partial t} + \nabla \cdot (\rho \mathbf{v} T) = \nabla (\frac{\lambda}{c_p} \nabla T) + \rho \frac{\lambda}{c_p^2} \left[\sum_{i=1}^{n_s} \frac{c_{pi}}{Le_i} \nabla Y_i + \nabla c_p \right] \nabla T$$
$$- \frac{1}{c_p} \left[\sum_{i=1}^{n_s} \omega_i h_i - \frac{Dp}{Dt} - \dot{q}_r \right]. \tag{2.14}$$

c_p is the specific heat capacity at constant pressure. The Lewis numbers Le_i are defined by

$$Le_i = \frac{\lambda}{\rho D_i c_p} \tag{2.15}$$

and describe the ratio between thermal diffusion $a = \lambda/(\rho c_p)$ and effective diffusion. D_i represents the diffusion coefficient of species i. In order to take