Part I.

Book part. e.g. "Solid fuel conversion kinetics"

CHAPTER 1

Gas phase kinetic modelling

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Abstract
Oxy-fuel combustion provides several significant advantages, such as a high CO_2 content and reduced NO_x emissions. The aim is to provide skeletal chemical kinetic models for the gas phase that can be coupled with a detailed solid particle model to describe coal and biomass solid fuel combustion under oxy-fuel conditions. Extensively validated detailed chemical kinetic models are applied and reduced in a multi-step reduction approach to develop skeletal kinetic models for the gas phase kinetic of coal and biomass combustion. The obtained chemical kinetic models are validated according to their reduction goal for the application in simulations under fuel-lean, high temperature, and atmospheric pressure conditions. To analyse NO_x formation, a NO_x sub-model is developed to be coupled with a detailed solid particle model for nitrogen release. Considering all volatile species requires an accurate prediction of main NO_x formation pathways as well as the C_5H_5N-chemistry.
The validation results of the developed kinetic models show an overall good agreement with the respective experimentally data for all targets of the respective developed kinetic model.

1.1. Introduction

Chemical kinetic models are essential when dealing with combustion phenomena as they provide crucial information regarding reaction rates, species transport, and temperature effects. Numerical simulations are performed to analyse the partially premixed flame resulting from the combustion of solid coal and biomass particles. Like in Chapter **B3**, where solid particle DNS are performed to analyse the combustion and ignition behaviour as well as the main NO_x formation pathways. These numerical simulations are conducted predominantly under high-temperature air and oxy-fuel conditions at atmospheric pressure. Therefore, with this application in mind, it is necessary to develop a chemical kinetic model to describe the underlying chemistry of the released volatile species in the surrounding gas phase of the solid particle. The volatile species are determined by employing the solid particle model for coal and biomass devolatilisation from Chapter **A8**, which leads to the definition of a complex mixture ranging from light hydrocarbons and oxygenated species up to heavy lignin tars ($C_{24}H_{28}O_4$) and aromatic compounds. Considering the NO_x sub-model from Chapter **A8**, various nitrogen-containing species are released to the gas phase, and the introduction in the kinetic model of the relevant chemistry describing their evolution in the combustion system is essential for accounting for the main NO_x formation pathways.

Detailed chemical kinetic models aim to describe the combustion process as accurately as possible. However, this might require hundreds or even thousands of species and reactions. Since the computational cost of complex simulations typically increases as the number of species in the employed kinetic model grows, developing skeletal kinetic models with a reduced number of species and reactions, while preserving high accuracy, is of key importance for performing the simulations that would be otherwise computationally prohibitive. According to the literature, present kinetic models for coal and biomass combustion are either not adapted to the solid particle model from Chapter **A8**, do not contain large aromatic species, or are not validated for the application under oxy-fuel conditions [**Shamooni2021**, **Goyal2017**, **Lovas2013**]. In addition, most of the kinetic models for NO_x formation do not contain all the volatile species released from the solid nitrogen particle model like the model from Glarborg et al. [**Glarborg2018**] or are not well documented [**Shamooni2021**].

The development of chemical kinetic models for the gas phase kinetic coupled with the solid particle model from Chapter **A8** is presented in this chapter. The first part delves into the development process of skeletal coal and biomass combustion models and a modular NO_x model. The second part focuses on validating these chemical kinetic models.

1.2. Chemical kinetic model development

The development of chemical kinetic models for coal and biomass combustion is presented in this section. A reduced version of the model from Cai et al. [**Cai2020**] is developed for coal combustion. According to this model, the development of recent kinetic models for coal and biomass combustion is discussed. These recent developed models are built to be adapted to the solid particle model from Chapter **A8**. Furthermore, a modular NO_x model is developed based on the solid particle model and is presented at the end of this section.

1.2.1. Development of skeletal coal and biomass models

A skeletal kinetic model for coal combustion is developed by Cai et al. [**Cai2019**]. The model from Cai et al. [**Cai2019**] is based on a kinetic model from Blanquart et al. [**Blanquart2009**] to describe the oxidation of a set of C_0 to C_4 hydrocarbon fuels including CH_4. This base-chemistry is extended to include the formation of polycyclic aromatic hydrocarbon according to the study from Narayanaswamy et al. [**Narayanaswamy2010**] and is refined by incorporating the hydrogen mechanism from Burke et al. [**Burke2012**]. Further details about the development process can be found in Ref. [**Cai2019**, **Cai2020**]. The model from Cai et al. [**Cai2020**] is extensively validated for the combustion of fuels in air [**Cai2019**] and for the oxy-methane combustion [**Cai2020**]. This kinetic model will be named ITV-2019 and is developed and validated for the ignition delay time, the laminar burning velocity, and the extinction strain rate of CH_4 under air and oxy-fuel conditions. A description of the extinction strain rate measurements is given in Chapter **B1**. In comparison to the ITV-2019 model, recently developed skeletal kinetic models for coal and biomass combustion are tailored to the solid particle model from Chapter **A8**. These models are developed to predict the ignition delay time and the respective fuel chemistry to be employed to simulate the respective gas phase kinetics under high-temperature and atmospheric pressure conditions. The development of these recent skeletal kinetic models for coal and biomass combustion involves a multi-step reduction strategy using detailed chemical kinetic models. A schematic of the whole reduction strategy is summarized in Fig. 1.1.

According to the devolatisation model from Chapter **A8**, coal and biomass particles release a complex mixture of volatile species to the gas phase. One of the dominant volatile species released during coal and lignin combustion is anisole, while levoglucosan is the dominant volatile species released from cellulose combustion. To describe the ignition delay time of coal and biomass combustion, the chemistry of anisole and propionaldehyde is considered, the most dominant species released at particle temperatures where biomass ignites is observed, based on model simulations with the solid particle model from Chapter **A8**. However, these species are not included in the extensively valid-
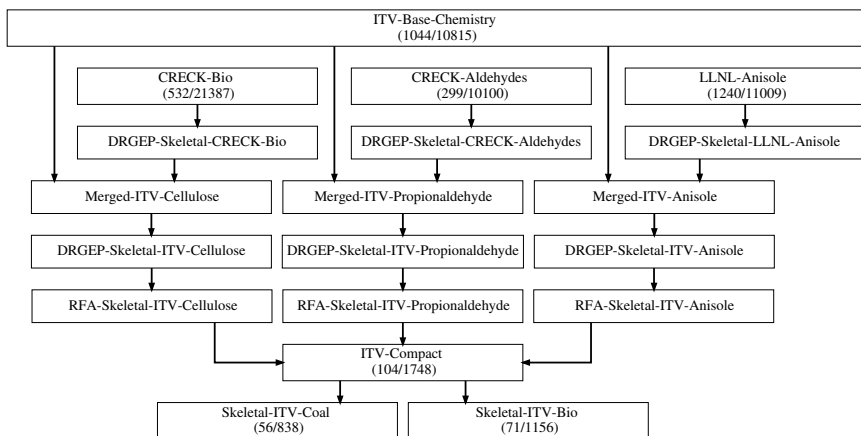
Figure 1.1.: Flow chart for developing the skeletal gas phase mechanisms for coal (Skeletal-ITV-Coal) and biomass (Skeletal-ITV-Bio) combustion. The initial mechanisms are the ITV-Base-Chemistry from Langer et al. [**Langer2023**], the CRECK-Bio [**Debiagi2016**], the CRECK-Aldehydes [**Pelucchi2015**], and the LLNL-Anisole model [**Wagnon2018**].

ated ITV-Base-Chemistry model [**Langer2023**]. To integrate these missing species chemistry in the model from Langer et al. [**Langer2023**], extensively validated detailed chemical kinetic models are used to describe the respective chemistry of interest over a broad range of conditions. The missing anisole chemistry has been adopted from the model of Wagnon et al. [**Wagnon2018**], cellulose volatile species from Debiagi et al. [**Debiagi2016**], and the propionaldehyde chemistry from Pelucchi et al. [**Pelucchi2015**].

The model from Langer et al. [**Langer2023**] has been systematically extrapolated from recently published chemical kinetic models and combined with these detailed chemical kinetic models [**Wagnon2018**, **Debiagi2016**, **Pelucchi2015**], describing the missing volatile species chemistry. The integration of the chemistry describing the gas phase kinetics of these volatile species into the model from Langer et al. [**Langer2023**] has been achieved using a systematic approach. In order to extrapolate only the relevant chemistry for the species, the Direct Relation Graph with Error Propagation (DRGEP) method [**PepiotDesjardins2008a**] has been applied to these detailed models. The obtained reduced chemical kinetic models are merged into the detailed model from Langer et al. [**Langer2023**] based on InChIs and SMILES for each species. Only the species and reactions, as well as the species thermodynamic and transport data, are extracted and added to the chemical kinetic model from Langer et al. [**Langer2023**], which are not included.

The so obtained kinetic models are referred to as "Merged-ITV-Cellulose", "Merged-ITV-Propionaldehyde", and "Merged-ITV-Anisole", as shown in

Fig. 1.1. The obtained models undergo a multi-step reduction strategy involving the DRGEP method [**PepiotDesjardins2008a**] and Reaction Flux Analysis. A reaction flux analysis allows a flexible and targeted extraction of major formation and consumption pathways of the species of interest from the mechanism, while the DRGEP method [**PepiotDesjardins2008a**] is a more conservative reduction method. The extraction with the reaction flux analysis is performed based on the respective validation cases to consider the range of validity and application. The validation database presented in Ref. [**Langer2023**] is expanded in this work by integrating additional speciation data representative of anisole oxidation [**Chen2022**], cellulose pyrolysis [**Norinaga2013**], and shock tube ignition-delay time measurements of anisole and propionaldehyde [**Pelucchi2015**, **AkihKumgeh2011**].

Skeletal kinetic models from each reduction step are named employing the prefixes "DRGEP-Skeletal" and "RFA-Skeletal" in Fig. 1.1, followed by the name of the corresponding detailed chemical kinetic model. The reduction process allows the retention of only the relevant chemistry for the species of interest. This allows the merging process of the skeletal models to be more straightforward, leading to a compact chemical kinetic model (ITV-Compact) able to accurately describe the evolution of the volatile species released from coal and biomass.

The final reduction step contains a DRGEP step and an additional reduction step using the reaction flux analysis to obtain skeletal chemical kinetic models for coal and biomass combustion. These skeletal kinetic models describe the gas phase kinetics of volatile species released from coal (Skeletal-ITV-Coal) and biomass (Skeletal-ITV-Bio). The applicability of both models can be emphasized by the fact that the Skeletal-ITV-Coal and the Skeletal-ITV-Bio mechanisms contain several volatile species released from the solid particle model from Chapter **A8**.

1.2.2. Development of a NOx chemical kinetic sub-model

To describe the formation of NO_x from nitrogen-containing volatile species released from the solid particle model from Chapter **A8**, a chemical kinetic gas phase model for NO_x formation is newly developed. This chemical kinetic model uses an ITV-NO_x model, a reduced version of the Glarborg model [**Glarborg2018**], crafted through ab-initio and experimental studies, as base chemistry. As a result of Girhe et al. [**Girhe2024**], the ammonia chemistry from the KAUST model is integrated into the ITV-NO_x model to improve the predictions of the ammonia chemistry. The C_5H_5N-chemistry to model tar-N is adopted from the CRECK-NO_x model [**Shamooni2021**] and integrated into the base-chemistry model.

A reaction rate modification is applied since this merged ITV-NO_x model over-predicts the NO formation over a broad range of experimental conditions. A rate parameter adoption from the CRECK-NO_x model [**Shamooni2021**] (reaction: $NCO + O \Leftrightarrow NO + CO$) and a minor tuning of the frequency

parameter (reaction: NCO+NO $\Leftrightarrow$ N$_2$O+CO) result in an accurate prediction of the NO chemistry (Complete-ITV-NO$_x$).

Next to the rate modifications, the nitrogen chemistry in the Complete-ITV-NO$_x$ model is extracted using the reaction flux analysis to obtain a more compact model size. Considering the validation cases from Alzueta et al. [**Alzueta2002**] and Wu et al. [**Wu2019**, **Wu2022**], a modular Skeletal-ITV-NO$_x$ kinetic model is obtained, which covers a broad spectrum of fuel-air ratios, temperatures, and initial conditions with 36 species and 595 reactions.

1.3. Validation of kinetic models

The skeletal chemical kinetic models are developed to predict the ignition delay time and respective fuel chemistry based on detailed chemical kinetic models. However, due to the reduction of detailed chemical kinetic models, the prediction accuracy of the chemistry of several species is affected. Consequently, a comprehensive validation is required to cover all relevant fuels and target species and include ignition delay times and speciation data in a broad range of temperatures at atmospheric pressure. Numerical simulations for the validation are performed using appropriate models in the FlameMaster code [**Pitsch1990**].

1.3.1. Skeletal kinetic models for coal combustion

This subsection provides a validation of the ITV-2019 kinetic model for coal combustion and the ITV-2023 models for coal and biomass combustion, covering all aspects of the respective development goals.

The ITV-2019 coal model is developed for an accurate prediction of the oxymethane chemistry. Figure 1.2 shows model predictions of the ITV-2019 model in comparison with experimental shock-tube measurements from Koroglu et al. [**Koroglu2016**]. Koroglu et al. [**Koroglu2016**] measures the ignition delay time for $CH_4/O_2/CO_2$ mixtures in bath gas of Ar for different pressures and equivalence ratios. As shown in Fig. 1.2, the ITV-2019 model satisfactorily predicts the ignition delay times for all conditions and temperature ranges.
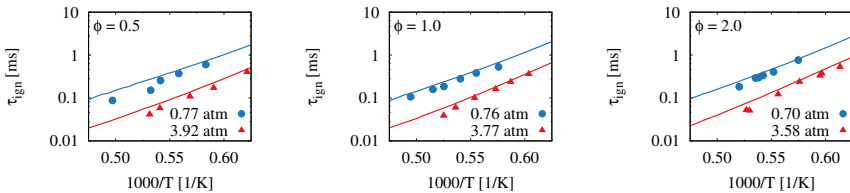

Figure 1.2.: Comparison of experimental measured ignition delay times of $CH_4/O_2/CO_2/Ar$ mixtures from Koroglu et al. [**Koroglu2016**] (symbols) with model predictions of the ITV-2019 model (lines).

Next to the ignition delay time validation, the ITV-2019 model is also validated for the extinction strain rate. Figure 1.3 compares the model prediction of the kinetic model with experimental measurements from Maruta et al. [**Maruta2007**]. Maruta et al.[**Maruta2007**] measures the extinction strain rate of diffusion flames with CH_4/CO_2 (300 K) and O_2/CO_2 (300 K) streams. The ITV-2019 model predicts the extinction strain rate in good agreement with the experimental data. Details about extinction strain rate experiments can be found in Chapter **B1**, and further validation cases, in-
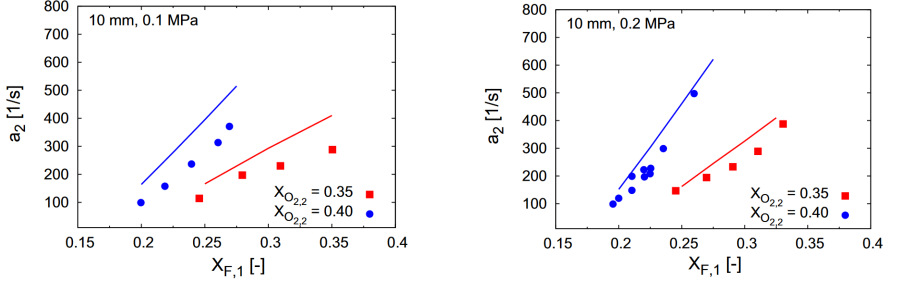
Figure 1.3.: Comparison of experimental measured extinction strain rates from
Maruta et al. [**Maruta2007**] (symbols) and model predictions of the
ITV-2019 model (lines).

cluding the laminar burning velocity, are presented in Ref. [**Cai2020**].
The ITV-2023 coal skeletal model is validated by considering the oxidation of
anisole at atmospheric pressure over a broad range of temperatures. Quant-
ities predicted by the skeletal model are compared against the ones of the
corresponding detailed model to assess the effect induced by the reduction
phase. Additionally, to assess the influence of differing base chemistry, the
performance of the ITV-based detailed chemical kinetic model is evaluated
against both the reference models and, where possible, experimental data.
The detailed chemical kinetic model from Wagnon et al. [**Wagnon2018**] and
the Merged-ITV-Anisole mechanism serve as a reference for the skeletal chem-
ical kinetic model in both cases.
Figure 1.4 compares the model prediction for the ignition delay time of an-
isole/air mixtures for the Skeletal-ITV-Coal, the Merged-ITV-Anisole, and
the LLNL-Anisole model [**Wagnon2018**] models. Model predictions for the
ignition delay times of the Skeletal-ITV-Coal and the Merged-ITV-Anisole
model are similar, indicating a low error in the mechanism reduction pro-
cess. The difference in the prediction of the ignition delay time compared
to the LLNL-Anisole model [**Wagnon2018**] is based on the different base
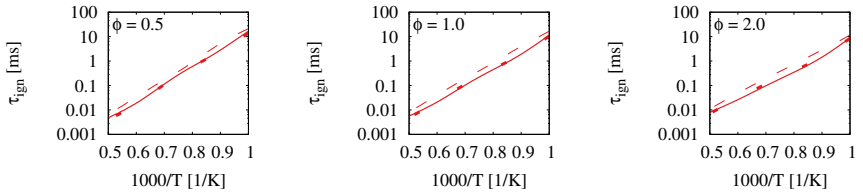

Figure 1.4.: Model comparison for the ignition delay times of anisole/air mixtures
at atmospheric pressure for the Skeletal-ITV-Coal model (solid lines),
the Merged-ITV-Anisole model (dotted lines), and the LLNL-Anisole
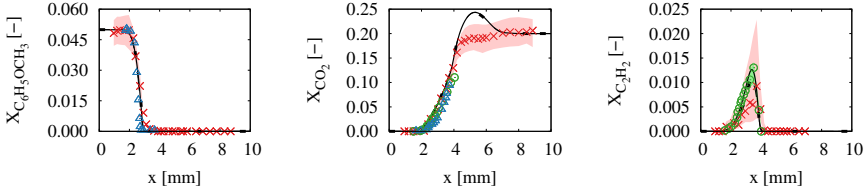model [**Wagnon2018**] (dashed lines).

Figure 1.5.: Comparison of experimentally measured mole fractions in the CO_2-O-Flame for anisole oxidation from Chen et al. [**Chen2022**] (ToF-MBMS: red crosses; GC-MS with a Rt-Q-Bond column: green circles; GC-MS with a DB-Petro column: blue triangles) with model predictions of the Skeletal-ITV-Coal (solid lines), the Merged-ITV-Anisole (dotted lines), and the LLNL-Anisole model [**Wagnon2018**] (dashed lines). Shaded areas with different colours indicate the measurement uncertainty of the respective techniques. x refers to the distance from the fuel inlet at 0 mm to the oxidizer inlet at 10 mm.

chemistry in the models. The validation of the anisole oxidation chemistry for the Skeletal-ITV-Coal model is given based on the experimental study from Chen et al. [**Chen2022**]. An examined flame configuration from Chen et al. [**Chen2022**] contains carbon dioxide as diluent on the oxidizer side (CO_2-O-Flame) to represent oxy-fuel conditions as discussed in Chapter **B1**. Figure 1.5 compares the Skeletal-ITV-Coal model predictions with the respective detailed kinetic model predictions in the CO_2-O-Flame. Anisole and CO_2 model predictions of the Skeletal-ITV-Coal model show no discrepancies to the detailed LLNL-Anisole [**Wagnon2018**] and the Merged-ITV-Anisole. Model predictions of the Skeletal-ITV-Coal model the intermediate hydrocarbon species C_2H_2 captures the GC-MS measured mole fraction peak, while the Merged-ITV-Coal and the LLNL-Anisole model [**Wagnon2018**] are both under-predicting the mole fraction peak.

1.3.2. Skeletal kinetic model for biomass combustion

Applying the newly developed skeletal kinetic model for biomass combustion requires a detailed validation of the ignition delay time and the levoglucosan and anisole chemistry in a predefined range of validity. The Skeletal-ITV-Bio model is built on the detailed chemical kinetic models of CRECK-Aldehydes [**Pelucchi2015**], CRECK-Bio [**Debiagi2016**], LLNL-Anisole [**Wagnon2018**], and the updated ITV-Base-Chemistry [**Langer2023**]. These detailed chemical kinetic models are validated against data from several experimental species over various conditions. The newly developed Skeletal-ITV-Bio kinetic model will be validated for the ignition delay time of propionaldehyde, secondary pyrolysis of cellulose volatile species, and for the anisole oxidation chemistry against experimental data [**Pelucchi2015**, **AkihKumgeh2011**, **Chen2022**].
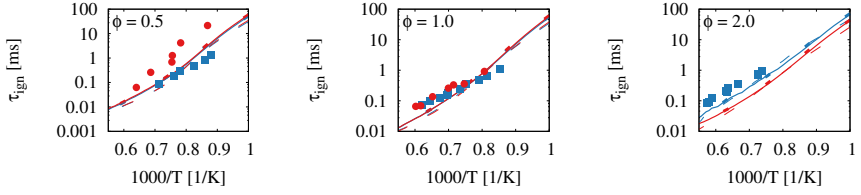
Figure 1.6.: Comparison of the propionaldehyde ignition delay time for experimental shock-tube measurements from Pelucchi et al. [**Pelucchi2015**] (blue squares) and from Akih-Kumgeh and Bergthorson [**AkihKumgeh2011**] (red circles) with model predictions of the Skeletal-ITV-Bio model (solid lines), the Merged-ITV-Propionaldehyde model (dotted lines), and the CRECK-Aldehydes model [**Pelucchi2015**] (dashed lines).

The ignition delay time for propionaldehyde is validated for three different fuel-air-equivalence ratios over a broad range of temperatures with experimental shock-tube measurements from Pelucchi et al. [**Pelucchi2015**] and Akih-Kumgeh and Bergthorson [**AkihKumgeh2011**]. Figure 1.6 compares the model predictions of the Skeletal-ITV-Bio model with the model predictions of the Merged-ITV-Propionaldehyde and the CRECK-Aldehydes model [**Pelucchi2015**] and with experimental measurements [**Pelucchi2015**, **AkihKumgeh2011**] for different equivalence ratios. No significant discrepancies are shown between the Skeletal-ITV-Bio and the Merged-ITV-Propionaldehyde for all validation cases, indicating that the mechanism development process introduced only a minor uncertainty in the ignition delay time prediction.

A model validation for the secondary pyrolysis of volatile cellulose species at different temperature levels is shown in Fig. 1.7 in comparison to the Merged-ITV-Cellulose and the CRECK-Bio model [**Debiagi2016**]. The initial conditions are based on the experiment by Norinaga et al. [**Norinaga2013**] using levoglucosan as balance for all species included in the experiment but not in
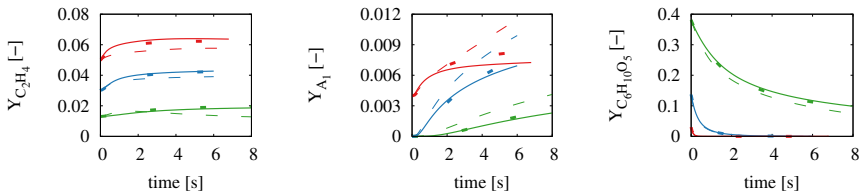

Figure 1.7.: Model comparison for the secondary pyrolysis of cellulose volatile species at $700\,^{\circ}C$ (green), $750\,^{\circ}C$ (blue), and $800\,^{\circ}C$ (red) for the Skeletal-ITV-Bio (solid lines), the Merged-ITV-Cellulose (dotted lines), and the CRECK-Bio model [**Debiagi2016**].
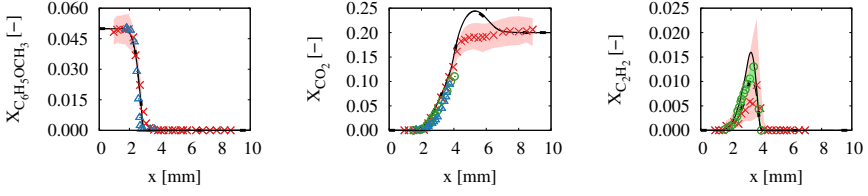
Figure 1.8.: Comparison of experimentally measured mole fractions in the CO_2-O-Flame for anisole oxidation from Chen et al. [**Chen2022**] (ToF-MBMS: red crosses; GC-MS with a Rt-Q-Bond column: green circles; GC-MS with a DB-Petro column: blue triangles) with model predictions of the Skeletal-ITV-Bio (solid lines), the Merged-ITV-Anisole (dotted lines), and the LLNL-Anisole model [**Wagnon2018**] (dashed lines). Shaded areas with different colours indicate the measurement uncertainty of the respective techniques. x refers to the distance from the fuel inlet at 0 mm to the oxidizer inlet at 10 mm.

the Skeletal-ITV-Bio model. Model predictions between the Skeletal-ITV-Bio and the Merged-ITV-Cellulose show only minor discrepancies. The discrepancies shown for A_1 between the Merged-ITV-Cellulose and the CRECK-Bio model [**Debiagi2016**] at higher temperatures result from the different base chemistry.

The lignin combustion part of the Skeletal-ITV-Bio model is validated with the anisole oxidation in the CO_2-O counterflow flame from Chen et al. [**Chen2022**]. Figure 1.8 compares the experimental measurements with the model predictions of the Skeletal-ITV-Bio model, the Merged-ITV-Anisole, and the LLNL-Anisole model [**Wagnon2018**]. Anisole and CO_2 mole fractions are well predicted with the Skeletal-ITV-Bio model, while the C_2H_2 formation is slightly over-predicted in comparison to the Merged-ITV-Anisole and the LLNL-Anisole model [**Wagnon2018**] as shown in Fig. 1.8.

1.3.3. NOx chemical kinetic sub-model

NO_x formation is validated for the Skeletal-ITV-NO_x model for the volatile species released from the solid particle sub-model described in Chapter **A8** in a predefined range of validity against experimental data [**Wu2022**].

Figure 1.9 compares the model predictions of the Skeletal-ITV-NO_x with the model predictions of the Complete-ITV-NO_x and the CRECK-NO_x model [**Shamooni2021**] and with experimental measurements for fuel lean conditions from Wu et al. [**Wu2022**]. The integrated C_5H_5N-chemistry shows no discrepancies, while the NO and NH_3 model predictions from the ITV-based models are closer to the experimental measurements under these conditions than the CRECK-NO_x model [**Shamooni2021**] predictions. Model predictions of the Skeletal-ITV-NO_x and the Compact-ITV-NO_x model show no discrepancies, indicating that the neglected pathways in the reduction step
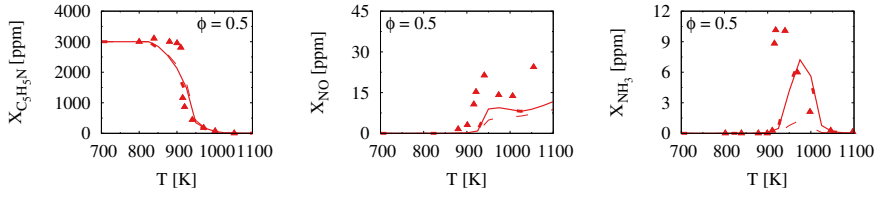
Figure 1.9.: Comparison of experimental data from Wu et al. [**Wu2022**] in a jet-stirred reactor (symbols) with model predictions of the Skeletal ITV-NO$_x$ (solid lines), the Complete-ITV-NO$_x$ (dotted lines), and the CRECK-NO$_x$ model [**Shamooni2021**] (dashed lines).

have only a minor error in the prediction accuracy of the target species.

Acknowledgement