HOPTIMAL

***H**ierarchical development of **OPTI**mised kinetic **M**echanisms for **A**dvanced combustion techno**L**ogies*

Promoter:

Professor Alessandro Parente

PhD student:

Andrea Bertolino

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0.1 Introduction

Nowadays our society massively relies on energy. Our lifestyles contribute to increase consumption, and the latter is estimated to grow of about 20% by 2040, as predicted by the U.S. Department of Energy information [1]. Simultaneously, the way we produce energy has a demonstrated impact over the environment: climate-change is affected by greenhouse gas production, particularly by CO_2 emissions. Attention must be paid also to other pollutants, such as NO_x and Soot, which cause photochemical smog/acid rains and climate warming/air pollution, respectively. In this framework, a significant adoption of renewable sources is expected in the future years, to meet the long-term objective of CO_2 neutrality and mitigate the effects of global warming. The intermittent nature of renewable sources requires, however, the development of storage solutions that can guarantee the availability of the required energy supply, when renewable sources are not available. Energy storage in the form of chemical compounds, sometimes indicated as Smart Energy Carriers (SEC), can lead to a true integration between renewable sources and existing infrastructure for energy conversion, such as combustion systems. Nevertheless, combustion science will need to undergo profound innovation, to promote novel technologies able to deal simultaneously with resources availability, and environmental impact, by avoiding pollutants formation at the source, rather than treat them downstream. Syngas, biogas, natural gas, hydrogen and ammonia enriched fuels are emerging, asking for the new technology to be fuel flexible. Moderate or Intense Low-oxygen Dilution(MILD) combustion [3] is a very promising candidate since it guarantees very large combustion and energy efficiencies, while suppressing both soot and NOx formation. From the chemical kinetics perspective, MILD combustion is a very challenging process to model. The well mixed conditions of the process imply that fuel conversion is chemically controlled, thus requiring detailed kinetic mechanisms to capture relevant phenomena. However, existing kinetic mechanisms have been developed for standard fuels and operating conditions. In presence of non-conventional fuel mixtures and technologies, as the one listed above, existing kinetic schemes need to be revised to properly account for diluted conditions, induced by recirculation or by the intrinsic to fuel composition. The objective of the present Thesis is to develop optimised kinetic mechanisms for application to realistic simulations of advanced combustion technologies in presence of non-conventional fuels.

0.2 State of the Art

MILD [3, 5] conditions allow suppressing NO emissions and hot spots, oxy-fuel combustion. Specific internal aerodynamic design in conjunction with high-velocity burners are responsible for the internal flue gases recirculation and turbulent mixing [3, 5]. This results in a localized reduction of O2 concentration, leading to a homogeneous and distributed reaction zone [2, 6] operating at

intermediate working temperatures. The latter characteristic is responsible for thermal NOx and Soot formation paths inhibition, other than creating ideal conditions for metallic materials longevity and reliability [2]. MILD combustion finds its major application field with steel industry, because it is suitable for fuel flexibility [7-13], and also for its capability to make CO_2 sequestration easier [4, 6]. This regime is still worthy of further investigations and attention, especially for the interaction between turbulence and chemistry. Recent Direct Numerical Simulations (DNS) [19] confirmed the need for non-flamelet approaches to deal with the frequent interactions between reaction zones in MILD combustion, advocating for novel canonical reactors for such a regime. Rapid compression machines were used to test the steam dilution effects on the ignition of hydrogen [20] and hydrogen, syngas, natural gas mixtures [21]. Steam effects on H2/O2 mixtures were also tested in a shock tube [22], and the same type of reactor was used to go through H2/CH4 mixtures diluted in Argon [23]. Within the last three years, shock tubes were widely used to test the effects of CO2 on ignition delay times for methane flames [24-27], syngas [28], and biogas [29]. Methanes auto-ignition delay times measurements with carbon dioxide [30], and N2 [31] dilution were performed in plug-flow reactors (PFR). The same was done to investigate nitrogen dilution influences propane ignition [32, 33], and how high concentrations of H2O/CO2 weigh on biogas chemistry [34]. Finally, Zhang et al. [35] investigated both experimentally and numerically the behaviour of CH4/CO2 mixtures, to assess the differences between real furnaces and ideal reactor simulations using Well-Stirred reactors (WSR), Lee et al. [36, 37] carried out review on existing experimental kinetic data for syngas and biogas in presence of carbon dioxide, water and nitrogen. Experimental data are crucial to understand the kinetic role of diluents such as CO2 and H2O, especially in third body reactions [30, 34], and to assess the uncertainty related to currently employed kinetic parameters, in particular collision efficiencies, whose knowledge is crucial in low-temperature combustion [38, 39]. Other open issues in MILD regime concern the formation of pollutants. Indeed, unconventional routes, such as N2O [2] and NNH intermediate [40, 41, 42] drive NOx formation, since thermal NOx is inhibited by the reduced temperatures. Within the present project, predictive simulation tools and experimental data will be coupled with a methodology for Uncertainty Quantification (UQ) [43, 44]. This aims at identifying the key parameters requiring revision and optimisation in presence of non-conventional fuels and technologies. The availability of experimental observations, with clear uncertainty bounds, is key to reduce the uncertainty associated to predictive models and their associated parameters, and improve the confidence in the results. The optimised kinetic schemes will be obtained from ideal reactor configurations, spanning a large range of operating conditions and fuel compositions, and later compressed using reduction method (i.e. Directed Relation Graph) [45-47] to describe turbulence/chemistry interactions in realistic combustion systems, where the use of detailed kinetic schemes is still computationally prohibitive.

0.3 Research Project

The research project consists of four main work-packages (WPs):

WP1: Exp. data collection and kinetic mechanism assessment. This WPI will focus on the collection of experimental data for the subsequent development and validation of kinetic models. The latter will include data from RCM,shock tubes, PFR, WSR and laminar flames, using syngas, biogas, natural gas and hydrogen (and Ammonia) enriched fuels, in presence of high CO_2 and H_2O dilutions (to simulate MILD-like conditions). Simulations will be carried out using OpenSMOKE++ [48]. In particular, the analysis will focus on the investigation of the chemical effect of diluent species such as CO_2 and H_2O affects the reactions, as third bodies with high collision efficiencies, and directly participating to a number of reactions. Local and global sensitivity will be used to identify the reactions mostly contributing to the model predictions, on which the subsequent uncertainty quantification (UQ) analysis will focus.

WP2: UQ, reduction and optimisation of detailed kinetic mechanisms. The information obtained in WP1 concerning the sensitivity of target quantities will be coupled to the uncertainties factors associated to the different kinetic steps, available in chemistry database. This will allow determining the most impactful kinetic parameters to be included in the UQ and optimisation process. Within the UQ process, the objective is to determine the range of input parameters of the most impactful ones, at which the numerical models produce results that are consistent with the experimental observations. The kinetic mechanisms issued from the UQ analysis will be then reduced to allow their application in the simulation of realistic combustion devices. Indeed, the use of comprehensive schemes for realistic configurations is still computationally prohibitive, given the large number of species and reactions involved. Methods like Directed Relation Graph (DRG) will be employed to reduce the number of species and reactions in the kinetic mechanisms. DAKOTA (dakota.sandia.gov) will be used for UQ and optimisation. The OpenSMOKE++ suite will be used for the reduction of the kinetic mechanisms.

WP3: Validation on pilot-scale obtained data and thesis writing. The optimised kinetic mechanisms will be validated on laboratory and pilot scale combustion systems. In particular, ATM research group at ULB will provide experimental data from a MILD combustion chamber. The furnace is fired with a 20kW nominal self-recuperative burner by WS GmbH, with a parallelepiped reverse-flow chamber (1x1 m^2 cross section). In terms of fuel compositions, the system disposes of a computer-controlled fuel blending system (from pure bottles). This will allow investigating the combustion features of the same non-conventional fuels investigated in WP1, as well as the effect of diluents (CO_2 and H_2O), closing the loop.

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