

MECHANICAL ENGINEERING / PHYSICS /  
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HERITAGE / STRUCTURAL, SEISMIC AND  
GEOTECHNICAL ENGINEERING / URBAN  
PLANNING, DESIGN AND POLICY / AEROSPACE  
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CHEMICAL ENGINEERING / INFORMATION  
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MATERIALS ENGINEERING / MATHEMATICAL  
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## DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

Coordinator:  
**Prof. Alessio Frassoldati**

### The Reference Committee

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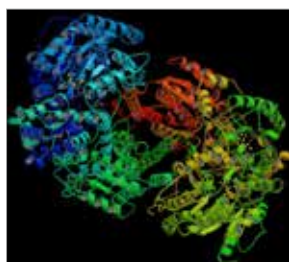
Alessandra Beretta, Giulia Bozzano, Elisabetta Brenna, Valentina Busini, Carlo Cavallotti, Francesco Cellesi, Alberto Cuoci, Alessio Frassoldati, Maurizio Galimberti, Francesco Gatti, Luca Lietti, Matteo Maestri, Davide Manca, Marco Mehl, Andrea Mele, Pierangelo Metrangolo, Massimo Morbidelli, Davide Moscatelli, Isabella Nova, Carlo Punta, Giuseppe Resnati, Selena Sironi, Giancarlo Terraneo, Enrico Tronconi.

### Grants

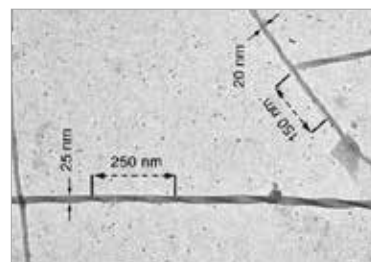
Pirelli, Captive Systems, Humanitas, EU H2020-MSCA-ITN-2014.

The Doctoral Program in Industrial Chemistry and Chemical Engineering (**CII**) is designed for students aiming to get a deep expertise on chemical processes and on material processing either as the inherent *research* or in the *process design and development* activities.

The program is the ideal extension of the *Laurea Magistrale* degrees in *Chemical Engineering*, *Safety and Prevention Engineering*, *Materials Science*, *Material Engineering*, *Industrial Chemistry and Chemistry*, **but it is also open to graduated in other scientific disciplines.**



Structure simulation of Nitrogenase enzyme for  $N_2$  conversion to  $NH_3$

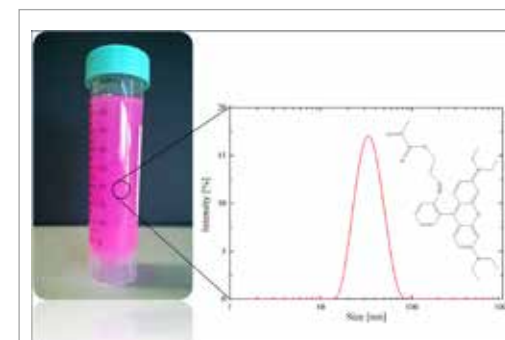


Amyloid peptide nanohelices in solution as ordered nanomaterials (Nature Commun. 2015, 6:7574, DOI: 10.1038/ncomms8574)

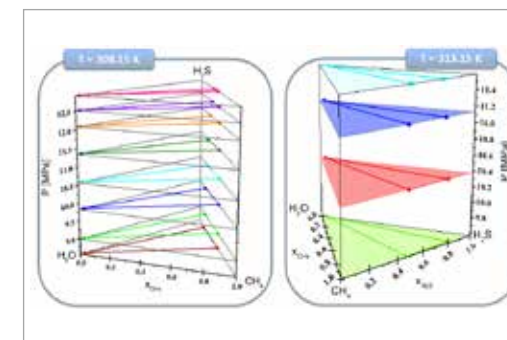
The general topic for the doctoral program in Industrial Chemistry and Chemical Engineering is the application of the chemical and physical knowledge to all the activities related to the synthesis, design, production and transformation of chemical substances and materials (like advanced inorganic, polymers and biomaterials). These studies involve not only the synthesis processes but also the related plants, here analyzed starting from the laboratory tests and the pilot plant experiments up to the industrial size ones, always including the careful evaluation of the related energetic, safety and environmental issues.

The final goal is to provide to the PhD student the tools and the skills: (1) to design and manage industrial processes at any size scales; (2) to develop new technical applications and (3) to create and to characterize new products and services.

The **CII** program covers three years for an overall amounts of 180 credits. The responsibility of the organization and of the contents of the doctoral program is attributed to the Professors Committee (PC). At the beginning of the Doctoral program, a tutor and a thesis advisor is assigned to each student. The tutor has a supervisor function during the whole doctoral program, whereas the thesis advisor is responsible for the thesis work.

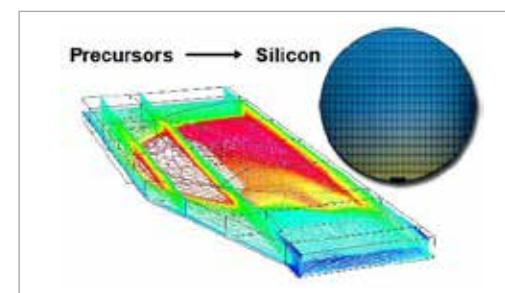


Biocompatible polymer nanoparticles functionalized with a fluorescent dye for in vivo imaging studies



VLE and VLLE measurements for the system  $CH_4$ - $H_2S$ - $H_2O$ .

The PC defines a specific curriculum for each student, on the basis of the tutor suggestions. The curriculum has to be designed in order to both cover deficiencies in the student scientific formation and to give a high-quality technical and scientific preparation. Since 2001 (XVII cycle) the **CII** program graduated more than 100 students, being ~80% now working in industry and the remaining in the university or government research centers. These data demonstrate the great link existing between the performed researches and the industry. In fact, during the years, numerous the research topics were directly supported by industrial companies, like ENEL, LPE Epitaxial Technology, Bracco, Flamma, Mapei, Solvay Specialty Polymers, RSE, Isagro, Tecnimont, Biochemtex, Pirelli.



Simulation of a chemical vapor deposition reaction for silicon films deposition



Hazardous gas dispersion simulation from an industrial accident

## STRATEGIES TO EXPLORE ESTABLISHED POLYMERIZATION TECHNIQUE FOR NOVEL APPLICATIONS

Ghobad Bagheri - Supervisor: Prof. Tiziano Faravelli

Forecasting the global energy demand is remarkably important for future energy policy and security. Considering various scenarios for world energy production and demand, the role of natural gas in shaping future energy demand will be notable, derived by its environmental advantages and versatility relative to other combustible fuels. This work is in the context of Combustion for Low Emission Application of Natural Gas project (CLEAN-Gas) funded by European Union's Horizon 2020 research and innovation programme under Marie Skłodowska-Curie Innovative Training Network (ITN), aiming to propose an innovative approach to improve natural gas combustion in industrial processes including detailed chemistry and computational fluid dynamics. Towards the goal, this work aims to extend the knowledge on hidden aspects of natural gas in the low environmental impacts combustion technologies through the development of comprehensive, detailed kinetic mechanism with predictive capabilities in a wide range of operating conditions of interest for real systems.

The kinetic mechanism of natural gas ( $C_1$ - $C_3$  fuels) describing the oxidation and combustion of natural gas is conceived and developed in a modular and hierarchical approach. This thesis is an effort to fill the

pressing need of a reliable and widely validated kinetic mechanism, specially developed for modern combustion systems with near-zero emission. More than 200 different experiments containing more than 6000 data points of various apparatuses such as plug flow reactor (PFR), Jet stirred reactor (JSR), shock tube, and 1-D laminar flame are collected from literature for the sake of extensive and critical model comparisons. This database is the most extensive set of experimental data available, which is beneficial for understanding the complex combustion processes of modern combustion technologies that have been hindered from successful integration into the industry.

A systematic study is performed on the combustion characteristics, less-known aspects and critical reaction pathways involved in MILD and oxy-fuel combustions. Diluent effects are evaluated in detail, and it is noteworthy to highlight that physical and chemical effects of diluent on the reactivity, laminar flame speed, ignition delay time, and formation of products are strongly dependent on the operating conditions (temperature, pressure, and equivalence ratio). Therefore, the analysis of the dilution effects is very case sensitive, and the contribution of each characteristic may vary accordingly.

Both  $H_2O$  and  $CO_2$  dilution reduces the system reactivity. The effect of  $H_2O$  is more notable due to chemical effects related to enhanced collisional efficiencies at the operating conditions of JSR experiments. On the contrary,  $CO_2$  has a higher impact on inhibiting flame propagation at higher temperatures, mainly due to the thermal and radical scavenging effects. Moreover, the effect of  $CO_2$  addition on methane ignition delay times is very marginal. The most likely explanation is that  $CO_2$  is scarcely reactive during the ignition, because of its stability, it does not actively modify the pool of radicals.

Finally, despite the satisfactory model prediction and reasonable agreement shown, the underlying impact of rate parameters uncertainty on model prediction is still not negligible. It has been shown that even if the kinetic mechanism is complete and free of any missing reaction pathway, rate

coefficient uncertainties generally precludes the possibility of predicting relevant combustion properties in some peculiar conditions. One of the primary reasons has been the lack of general agreement as to how to move forward in obtaining a comprehensive, unified and predictive model for fuels combustion.

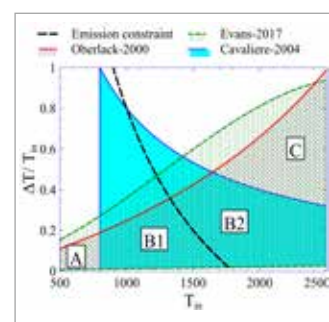


Fig. 1

# NUMERICAL MODELING OF SOOT FORMATION AND EVOLUTION IN LAMINAR FLAMES WITH DETAILED KINETICS

Agnes Livia Bodor - Supervisor: Alberto Cuoci

An image appearing when the phrase soot is heard is the smoke emitted by an exhaust pipe. The imperfect combustion of hydrocarbon fuels is a source of this harmful pollutant. The industrially controlled combustion of hydrocarbons can provide the carbon black, an industrial product widely used in our everyday life. For both its utilization and its harming effect, the surface of these combustion generated particles plays an important role, therefore, it is of interest to possess information on the particle morphology beside its mass or volume.

Soot particles were found, at various conditions, to have a fractal-like structure built up from spherical shape building blocks, so-called primary particles. This increased interest in the particle surface and its evolution gives the motivation to extend numerical models to provide related information, i.e. particle surface or primary particle size. Furthermore, as the primary particle size influences the chemical and collisional processes, accounting for this parameter can improve the model predictions.

The requirements for numerical models are various depending on the purpose of the simulation. Multidimensional laminar flames, like a laminar coflow diffusion flame, are less complex than flames of industrial combustion systems. However, the soot formation

processes are analogous in the two cases, therefore, the investigation of these flames are of interest. In order to obtain a detailed description of the chemical processes, while keeping the computational cost in these flames at an affordable level, using chemical discrete sectional models is a suitable choice. As in their current version, these models do not provide information on the primary particle size their development in this direction is of interest.

Guided by the above motivation, a numerical strategy to determine the primary particle size is presented in the context of the chemical sectional models. The proposed strategy is based on solving the transport

equation of the primary particle number density for each considered aggregate section.

In order to validate numerical primary particle size, the comparison to experimental data is required. Due to its numerous advantages, the Time-Resolved Laser-Induced Incandescence (TiRe-LII) technique is a nowadays popular experimental method. However, the comparison of the numerically and the experimentally obtained primary particle size may be charged with uncertainties introduced by the additional measurements or assumptions of the numerous parameters required to derive primary particle size from the detected signal.

In order to improve the validation strategy, an additional approach for primary particle size distribution validation with TiRe-LII is proposed. This is based on the reconstruction of the temporal evolution of incandescence from the numerical results and its comparison with the measured signal. The effectiveness of this 'forward' method is demonstrated a priori by quantifying the errors potentially avoided by the new strategy.

The validity of the proposed primary particle tracking model is tested by both the traditional 'inverse' and the 'forward' method on target flames of the International Sooting Flame (ISF) Workshop. In particular a laminar premixed ethylene flame is considered first. Then, two laminar coflow ethylene flames with different dilutions are put under the scope. The improvement of the mean primary particle size prediction by the new model (PPT) compared to the formerly used assumptions, like assuming spherical particles or constant primary particle size in the aggregates, was proven, see Figure 1. The sensitivity to the model parameters, such as accounting for the surface rounding and the choice of smallest aggregating particle size, is explored in both the premixed flame and in the coflow flame with highest ethylene content.

To understand the effect of the

fuel stream dilution on the primary particle size in the coflow flame, first, the flame-flow interaction and the effect of the dilution on the flame structure is investigated. Then, the correlation between the temperature, the precursor concentrations, the soot volume fraction, and the primary particle diameter is examined. Finally, the formation rates and the residence time along the particle trajectories are studied to understand the effect of dilution on the spatial localization of the biggest particles along the flame.

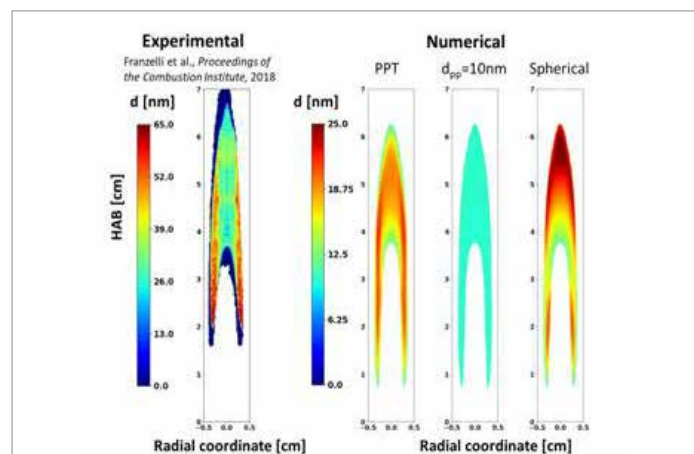


Fig. 1 - Experimentally an numerically determined primary particle size in the richest investigated coflow ethylene flame, numerically by the proposed model (PPT), by assuming constant 10 nm primary particle diameter ( $d_{pp}$ ) in the aggregates and by assuming spherical particles.



# MULTISCALE DESIGN, INTEGRATION & OPTIMIZATION OF BIOREFINERIES FOR THE PRODUCTION OF LIQUID FUELS

Andre Furtado Amaral - Advisor: Prof. Flavio Manenti

Biorefineries have been conceptualized to substitute the traditional oil refineries, producing heat, electricity and chemicals (among which, liquid fuels) from biomass. Energy production from biomass has been proposed and re-proposed over the years in different processes. For some processes (as is the case of gasification) different sources have presented conflicting values for production costs. This may originate from a lack agreement in the typical size these plants would adopt at a commercial implementation of the process. Alternatively, differences in product cost may result from an overly simplified process assessment. In some new processes (as is the case of biogas), different process designs may result in more economic configurations. The potential reach of this technology is still not well understood. Maybe for this reason, biomass usage for energy production is an active area of research. In this work, these processes were studied from a multiscale perspective using computer simulations. Four different software were used: commercial process simulator Aspen HYSYS; energy integration software Aspen Energy Analyzer; GasDS, a gasification / pyrolysis simulator and the MATLAB programming environment. Lignocellulosic biomass gasification was described with the aid of a detailed phenomenological model.

In this model, biomass is considered a mixture of cellulose, hemicellulose and three surrogate compounds that account for the most abundant monomers in lignin. Biomass composition was determined from an innovative data fitting method based on Lagrange multipliers. The calculated biomass composition produces lower heating values (LHVs) that are consistent with experimental observations. The relative LHV error was not bigger than 10% for any of the biomasses studied. The developed method represents an improvement from the previous 'triangle model', especially because it uses experimental information in a more systematic approach to quantify biomass composition. An entrained flow gasifier was simulated using a detailed,

phenomenological model, implemented in the GasDS software. The software is an in-house developed computer package that has been extensively validated in different configurations. The model considered a kinetic mechanism based on the above mentioned results on biomass composition to successfully predict biomass conversion and syngas yield for a given oxygen consumption. Almond shells and olive pits were the two biomasses with the biggest syngas yield per oxygen input, with a value of 314 mol syngas / mol . Biomass conversion values compared well with experimental values and were close to chemical equilibrium. The simulator displayed numerical instabilities during the unsteady state operation, due to the strategy used to increase the step size. This effect

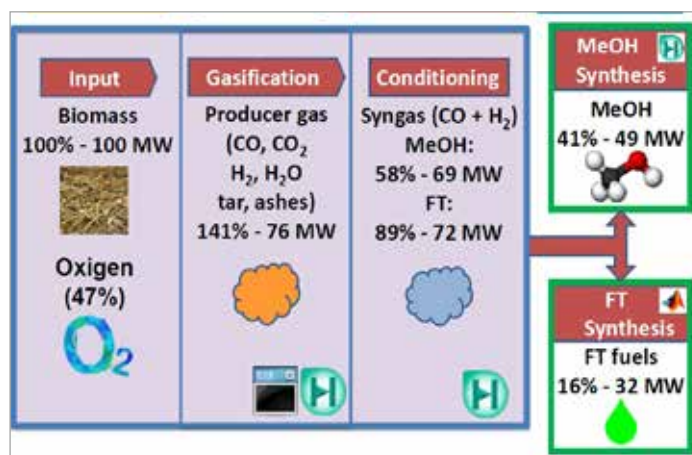


Fig. 1 - Scheme detailing the gasification processes.

is not present during steady state operation and, therefore, does not influence these results. The coproduction of heat, electricity and chemicals from second-generation biomass was assessed. Two different scale sizes were considered, with biomass lower heating value inputs of 1 and 100 MW, respectively. These scales are representative of decentralized and centralized production concepts, each of which with its own characteristic transformation pathways. For the centralized concept, biomass gasification was considered. Two final uses for syngas were considered: production of methanol and production of Fischer-Tropsch (FT) fuels. The FT product distribution model considered olefin readsorption and it was solved using an innovative power series solution. Methanol production is the superior process, both in economic and in terms of final conversion to liquid fuels. The economics of the Fischer-Tropsch process suffers due to the low energetic yield of the reaction in

terms of high valued liquid products. It remains to be confirmed (1) whether if the correlations used are adequate to represent the FT reaction system and (2) if further income could be expected if the other reaction products could be sold as high value products. Both processes are economically unfeasible, with product costs that range (approximately) from 60 to 90 €/MWh (MeOH) and 80 to 210 €/MWh (FT). Even so, methanol production is an interesting alternative to current biogas concepts. The minimum subsidy cost of this process ranges from half to one third of current biogas subsidy costs. Figure 1 summarizes the results of this analysis. The decentralized utilization concept considers the anaerobic digestion of biomass for the production of biogas. Three biogas processes were assessed: HPC (biogas to methanol), BioCH<sub>4</sub> (biogas to biomethane) and CHP (biogas to heat & electricity). The last two processes are already used commercially with the aid of subsidy policies. The economic analysis

indicates that, without these policies, none of these attain self-sustainability due to high overall manufacturing costs; the estimated minimum support cost (MSCs) were 108, 62 and 110 €/MWh for the HPC, BioCH<sub>4</sub> and CHP processes, respectively. The model could explain currently practised government subsidies in Italy and Germany. It was seen that the newly proposed HPC process is economically comparable to the traditional CHP process. Therefore, the HPC process is a possible alternative to biogas usage. A subsidy policy was proposed: 50, 66, 158 and 148 €/MWh for available heat, methane, electricity and methanol (respectively). The proposed policy results in a 10% OpEx rate of return for any of the processes, thus avoiding a disparity in the production of different products. Figure 2 summarizes the results of this analysis. The economic assessment in this work is certainly insightful in revealing the importance of the support policies on the short- and medium-term survival of such processes. Other than the obvious environmental aspect, these processes are fundamentally associated to the valorization of biomass. Process economics could be enhanced if part of the biomass were elaborated into acetic acid or any other high-valued chemical. This could be the missing elements with which to make such processes economically self-sufficient. These measures could effectively enable the establishment of a new productive model, reducing dependence on fossil imports while promoting social and economic development.

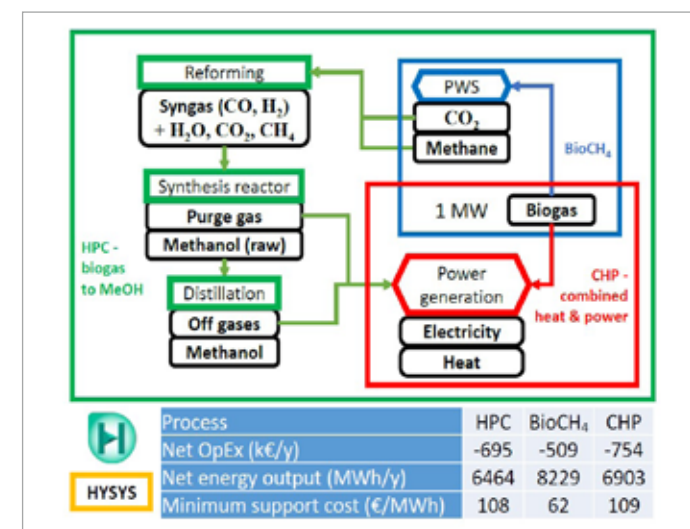


Fig. 2 -Scheme detailing the biogas processes.

# POLLUTANT PREDICTION IN NUMERICAL SIMULATIONS OF LAMINAR AND TURBULENT FLAMES USING VIRTUAL CHEMISTRY

Giampaolo Maio - Supervisor: Prof. Alberto Cuoci

The two main drawbacks of combustion processes involved in energy conversion devices are: the contribution to global warming and the pollution of industrial and urban areas. The energy sector, production, transformation and the use of energy, is central for the climate change challenge. It accounts for around two-thirds of global Green House Gases (GHG) emissions and about 90% of carbon dioxide (CO<sub>2</sub>) emissions, most prevalent GHG. The CO<sub>2</sub> emissions are directly related to the efficiency of the combustion devices and to the type of fuel that is used in the combustion process. Hence, improving the efficiency of the combustion devices and looking for cleaner fuel such as natural gas are the main objectives to pursue. Instead, to improve the local air quality (especially in the urban and industrial areas) the reduction of pollutant emissions from combustion processes is of paramount importance. Combustion engineers use numerical simulation to design and optimize combustion devices to improve their efficiency and to reduce pollutant emissions. CFD (Computational Fluid Dynamic) simulation, applied to the solution of complex combustion processes, has made significant efforts in recent years, allowing the simulation of real scale combustion chambers. The accurate reproduction of pollutant formation (CO, NO<sub>x</sub>,

unburnt hydro- carbons, etc...) and inner flame structure prediction in turbulent flame simulations, at an affordable CPU cost, is still a research topic of interest and that needs to be fully addressed and better understood. In line with the combustion modeling challenges described above, the present research work focuses on the prediction of CO and NO formation in complex flame conditions at reduced CPU cost. Multi-modal flame regimes and flame heat losses are considered. Here, the words multi-modal stands for coexistence of premixed and non-premixed flame structures. In this thesis, CO and NO reduced chemistry models are developed using the recent virtual chemistry approach. Virtual chemistry is a reduced order model which aims to describe global flame quantities, temperature and pollutant formation. The strategy consists in designing virtual mechanisms composed of a reduced set of virtual species interacting through a reduced number of virtual reactions. Virtual species thermo-chemical properties and virtual reactions kinetic constants are optimized to target "real" flame properties of interest such as temperature, heat release and pollutant concentration. Virtual chemical mechanism is composed of one main mechanism and several satellite virtual sub-mechanisms.

In this work virtual mechanisms are developed and validated in 1-D laminar flame archetypes. Successively, their applicability to multidimensional laminar and turbulent CFD computations is shown, demonstrating the value of the approach. The multidimensional CFD results are either validated versus experimental data for the turbulent test cases or compared to fully detailed chemistry computations for laminar configurations. Compared to previous literature works, the validity domain of the virtual chemistry approach is further broadened. The virtual chemistry applicability to multi-dimensional CFD computations at reduced CPU cost, is further demonstrated. In particular, virtual chemistry is

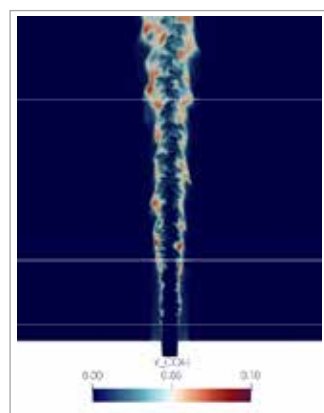


Fig. 1 - Carbon monoxide (CO) prediction in Sydney inhomogeneous piloted burner from a 3-D LES computation.

challenged and validated in the LES (Large Eddy Simulation) context in two turbulent flame configurations to predict CO emissions:

- 1) Sydney inhomogeneous piloted burner: representative of multi-modal turbulent flame conditions. Figure 1 shows the CO field predicted by the 3-D LES numerical simulation using the new virtual chemistry model optimized to recover multi-modal flame conditions.
- 2) Preccinsta burner: a semi-industrial confined flame impacted by wall heat losses. Figure 2 shows the CO field predicted by the 3-D LES numerical simulation using the new virtual chemistry model optimized to recover non-adiabatic flame conditions. A new and original reduced order

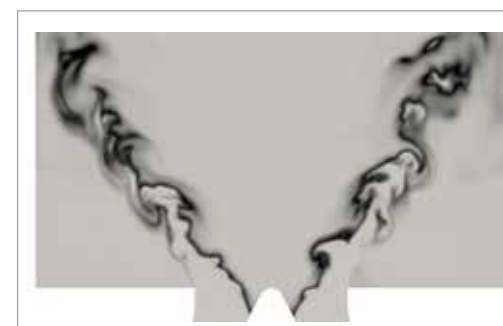


Fig. 2 - Carbon monoxide (CO) prediction in the Preccinsta burner from a 3-D LES computation.

kinetic model for NO (Nitric Oxide) prediction, based on the recent virtual chemistry methodology, is also developed in this work. To recover the chemical structure of multi-mode combustion, both premixed and non-premixed flamelets are included in the learning database used to optimize the virtual NO mechanism. A multi-zone optimization procedure is developed to accurately capture both fast and slow NO chemistry and reburning pathways. The proposed NO sub-mechanism and optimization methodology are applied to CH<sub>4</sub>/air combustion. Laminar 1-D premixed and non-premixed flamelet configurations are first tested. The approach is then further assessed in

2-D CFD laminar flame simulations, by providing a direct comparison against detailed chemistry. 2-D premixed, non-premixed and partially premixed flame configurations are numerically investigated. For all cases, the virtual mechanism fairly captures temperature and NO chemistry with only 12 virtual species and 8 virtual reactions with a drastic CPU time reduction (by a factor of 40) compared to detailed chemistry. Figure 3 shows NO emission prediction from numerical simulations for two different flame benchmarks: a premixed single slot burner (like a Bunsen flame) and a non-premixed coflow flame. Virtual chemistry results are directly compared to reference detailed chemistry ones.

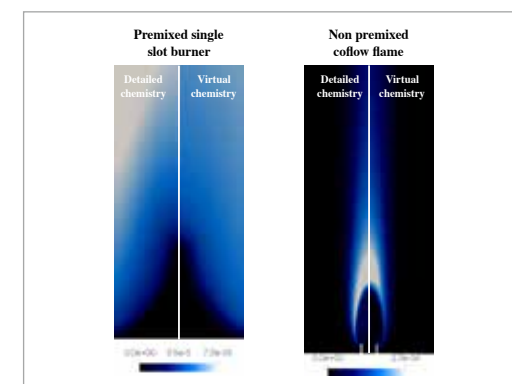


Fig. 3 - NO emission prediction in a premixed laminar 2-D flame (right figure) and in a non-premixed laminar 2-D flame (left figure). Virtual chemistry results are compared to detailed chemistry ones.

# CHEMICAL AND PHYSICAL PATHWAYS OF PAH AND SOOT FORMATION IN LAMINAR FLAMES

Warumporn Pejpichestakul - Supervisor: Prof. Alessio Frassoldati

Combustion of hydrocarbon fuels is a major source of pollutants, causing adverse effects to environment and human health. Combustion-generated polycyclic aromatic hydrocarbon (PAH) and soot particles are within the most abundant and harmful pollutants generated from burning of hydrocarbon fuels. Pollutant emission reduction not only is beneficial for the environment and human health but also to increase the efficiency of combustion processes. This work is in the context of Combustion for Low Emission Application of Natural Gas (CLEAN-Gas) project, European Union's Horizon 2020 research and innovation programme under Marie Skłodowska-Curie Innovative Training Network (ITN), aiming to propose an innovative approach to improve natural gas combustion in industrial processes including detailed chemistry and computational fluid dynamics. Towards this goal, the aim of this work is to characterize and understand the chemical and physical phenomena behind pollutant formation through the development of a comprehensive detailed kinetic mechanism with predictive capabilities in a wide range of operating conditions of interest for real systems. The kinetic sub-mechanisms describing PAHs and soot formation are coupled to the core mechanism describing smaller species gas phase combustion and pyrolysis kinetics. This work focuses

on the development of PAHs and soot sub-mechanisms and validate them in a wide range of operating conditions by means of extensive and critical comparisons with a large number of experimental data. The validation against the experimental data presented in this thesis mostly involves laminar flames using 1-D and 2-D simulations. Considering the difficulties in quantitative PAH measurements, an extensive data collection of rich premixed flames was carried out. This extensive database is beneficial for improving the reliability of kinetic models in a wide range of conditions. The effect of the soot formation was also quantitatively investigated using the developed kinetic model (Fig. 1), highlighting the importance of describing the interaction with soot to predict heavy PAHs concentrations.

The study of soot formation/oxidation pathways was performed using a discrete sectional model coupled with gas phase reactions and PAH sub-mechanism. The essential tool "SootSMOKE" was developed in order to generate the large soot sub-mechanism on the basis of rate rules and reaction classes. The effect of temperature-dependent collision efficiencies is also included in the model for soot formation due to their importance on particle size distribution. The collision efficiency for various particle size is studied and

compared with experimental data and molecular dynamics simulations for the PAH dimerization where the experimental data are not available. This kinetic model was validated in comparison with the premixed burner-stabilized stagnation ethylene flames at heavily sooting conditions. A model accounting for temperature and particle size dependence also provides a more general validity, especially on soot number density. Sensitivity analysis of different key parameters controlling coagulation rates is carried out to highlight impacts of each parameter on PSDFs. The characterization of the coagulation mode of PSDF strongly relies on the particle coagulation processes. The validation in laminar counterflow diffusion flames highlighted that physical properties affect the behavior of particles in

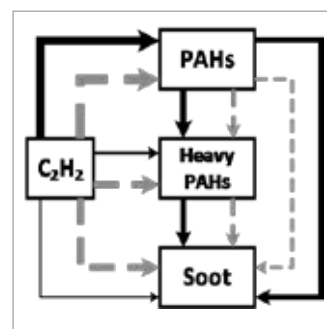


Fig. 1 - Relative contributions of HACA mechanism and PAH condensation reactions to the growth of soot particles at low (dashed lines) and atmospheric pressure (solid lines).

flames and are also important. The thermal diffusion of gaseous species and soot particles play a vital role in diffusion flames, particularly, to characterize the particle stagnation plane, which was experimentally observed.

The detailed kinetic model of PAH and soot formation developed in this thesis work has been further validated using the experimental measurements obtained in a comprehensive study of laminar premixed flame which follows the transition of gas-phase to soot particles. However, this flame is characterized by the presence of a significant buoyancy, which influences the convective flow field (Fig. 2). Therefore, 2-D simulation is required to study this flame. This investigation highlighted that not only the accurate description of chemical and physical properties is important, but the appropriate simulation approach is also critical. An improper numerical simulation can lead to the misinterpretation of the kinetic model. Additionally, the model is able to characterize the

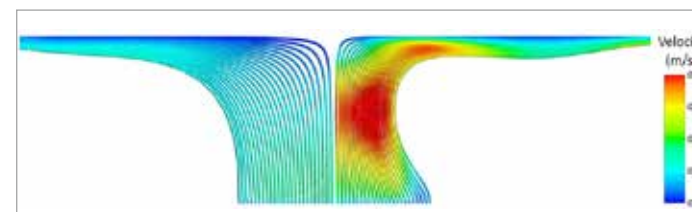


Fig. 2 - Stream lines calculated from the model accounting buoyancy (right) and the model neglecting buoyancy effect (left).

plateau behavior, which was observed experimentally for some aromatics in the post-flame region because of a counterbalancing effect between their formation from gaseous species and their consumption due to soot growth. Again, this confirmed that the validation of PAH without soot sub-mechanism is misleading in rich flames.

The overall validation clearly highlights the presence of critical gaps between the kinetic model and experimental studies of PAH and soot. The validation of PAH, soot precursors, is usually ignored during soot model development, while the inclusion soot model is also usually neglected during the PAH model development. To narrow the gap toward soot formation, the development of PAH and soot models should be carried out concurrently as the validity of the soot model cannot be assessed nor achieved without reasonable PAH prediction and vice versa. The concurrent study the formation of PAHs and soot formation requires more comprehensive

experimental studies using different flame configurations or measurement techniques, especially those that can be simulated using quasi 1-D simulation. This will allow a deeper understanding of chemical and physical pathways in PAH and soot formation.