SMARTCATs

2nd General Meeting

&

Workshop on Smart Energy Carriers in Industry

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Book of Abstracts

SMARTCATs / CM1404

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Smart Energy Carriers
Chemistry and Technologies

COoperation in Science and Technology (COST) is a European framework (www.cost.eu) that aim to create a networking to make people collaborate on a common research topic founded by national or international research projects and share competences and results in synergistic way.

The idea of SMARTCATs COST Action steams from the need to face with the continuos change of the energy scenario. Even if combustion based energy production will continue to play a major role, an energy production system shift will occur in the near future. The growing volatility of world's economies and politics which has characterized the past decades, in combination with increasing environmental concerns, has strongly affected and modified the fuel portfolio. Moreover, the availability of large amounts of variable renewable electricity (e.g. wind and solar energy) introduced in large amounts into the power system, requires the identification and the efficient use of energy carriers, which are chemical compounds produced as storage from electric energy surplus. On the other hand the spreading of energy production and distribution system based on a smart grid concept imposes the use of locally and diverse available sources.

These scenarios redefine the concept of fuel as smart energy carrier actually enlarging it to a much wider class of compounds. This category can include simple hydrocarbons, natural gas mixtures as well as low calorific fuels, 1st and 2nd generation biofuels, polymers which can be obtained from wood fatty acid methyl esters, hydro-treated vegetal oils etc.

Carriers to energy conversion technologies, from small/domestic scale to large power conversion systems as well as to engines, have to provide practical answers to satisfy the energy needs.

SMARTCATs COST Action is a pan european network of scientists and companies focused on the study of combustion of a vast palette of energy carriers finalized to the development and optimization of fuel flexible, efficient, advanced and emerging combustion technologies. The main aim is to allow the use of whatever available and suitable energy carrier in the best available combustion technologies.

During the annual Action general meeting, Action participants meet for sharing and discussing the latest knowledge gained on the conversion and use of energy carriers, spanning from the development and optimization of kinetic mechanisms for fuel conversion, to pollutants monitoring and control to the advanced diagnostics, from the generation of tools for data collection and mining to the application of smart energy carriers at large scale.

The approach to accomplish this aim is twofold. On the one hand, academic/research organizations will devote strong efforts to bring together fundamental/ advanced numerical and diagnostic tools to improve the understanding of combustion at micro/meso-scale levels.

On the other hand, the exchange between academic and industrial partners will support the optimization of tools developed in the Action exploiting the way that SECs could be utilised at the macro-scale in advanced combustion devices. This interaction will lead to the identification of standards and criteria for the development of internet tools devoted to integration of experimental and numerical physico-chemical combustion data. According to this methodology the SMARTCATs work programme is structured in five Working Groups (WG).
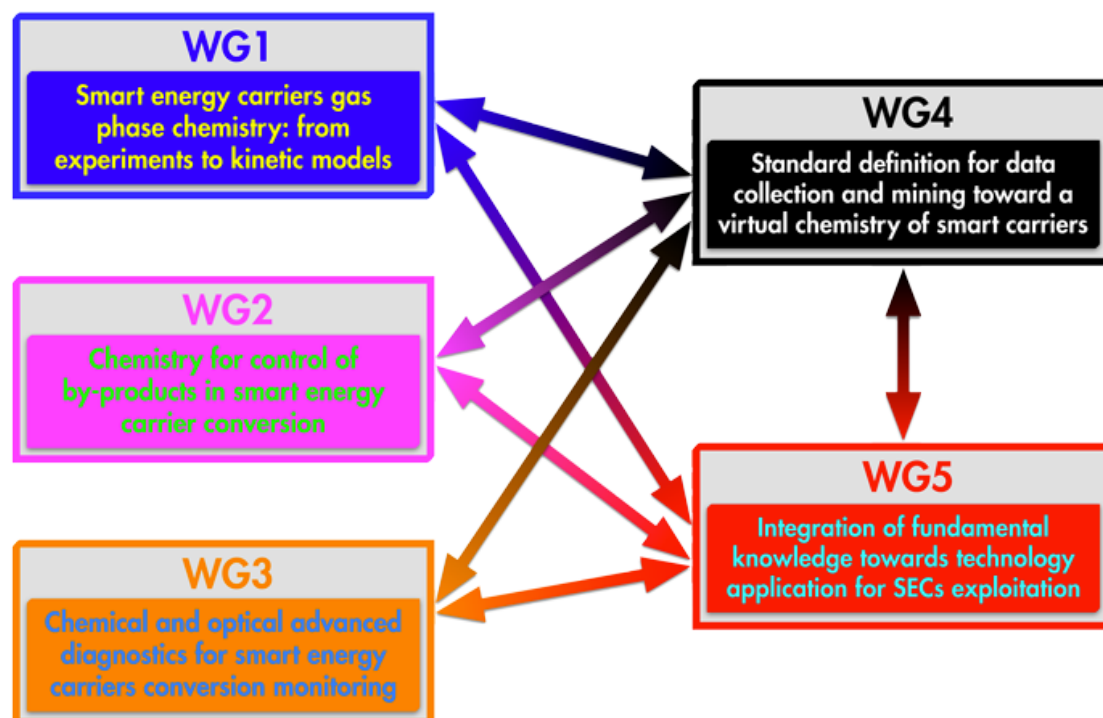
WG1. Smart Energy Carriers gas phase chemistry: from experiments to kinetic models that aims to improve the knowledge on detailed chemistry and thermochemistry for the combustion, pyrolysis, and oxidation of fuels, such as natural gas mixtures (compressed natural gas, liquefied natural gas, syngas natural gas, bio- methane), simple molecules (large normal and iso-paraffins, alcohols, esters, saturated and unsaturated cyclic ethers) that can be present in 1st and 2nd generation biofuels and complex mixtures of molecules actually found in 1st and 2nd generation biofuels or in the proposed surrogates

WG2. Chemistry for control of by-products in Smart Energy Carrier conversion that aims to increase knowledge on the formation of organic and inorganic combustion by-products. The pollutant tendency of smart energy carriers will be studied by tracing pollutant species typically formed in combustion (carbon monoxide, unburned hydrocarbons (UHC), polycyclic aromatic hydrocarbons (PAH), aldehydes, NOx soot and nano-particles) as well as other classes of pollutants possibly originating from SECs.

WG3. Chemical and optical advanced diagnostics for Smart Energy Carriers conversion and monitoring that aims to improve the knowledge on advanced combustion diagnostics, with a strong focus on technology transfer from fundamental to complex systems, and focuses on advanced sampling and chemical analysis diagnostics, laser-based and mass-spectrometric diagnostics in fundamental combustion devices and chemical kinetics experiments, elementary reaction rate measurements, chemical markers for combustion performance characterization, combustion and emission measurements in complex systems (engines, furnaces, household applications, etc).

WG4. Standard definition for data collection and mining toward a virtual chemistry of Smart Energy Carriers that aims towards the identification of the main requirements and tools for the development of databases, software and mathematical tools for data collection and handling as well as chemistry optimization using data mining techniques. Definition of 'crucial' experiments, numerical simulations and uncertainty and sensitivity analysis in combustion modelling will be key issues to be considered.

WG5. Integration of fundamental knowledge towards technology application for Smart Energy Carriers exploitation that is to apply/integrate the knowledge tools developed in WG1-WG4. This will provide optimized ready to use tools and techniques for an effective use of SECs on large scale. The research activities of the WG will be driven by the identification of validation test cases, identified in collaboration with the industrial partners to provide scale-bridging information from the laboratory units to the real applications by means of integration of detailed kinetic mechanisms in large scale numerical simulations, and assessment of the uncertainty related to numerical predictions for their use in new design and regulation.

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K. Van Geem, A. Gonzalez-Quiroga, H. Carstensen, G.B. Marin

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G. Sorrentino, P. Bozza, P. Sabia, R. Ragucci, M. de Joannon

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Woody Residues Torrefied and Pelletized at the Small Scale: a New Energy Carrier as a Replacement for Fossil Fuels

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J. Vávra, M. Takáts, I. Bortel, Z. Syrovátka

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SMARTCATs 2nd General Meeting - Workgroup 1
Chairs: F. Battin-Leclerc - CNRS and

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SMARTCATs 2nd General Meeting - Workgroup 2
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Physical chemistry of Combustion Processes and of the Atmosphere (PC2A), University of Lille Sciences and Technology

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SMARTCATs 2nd General Meeting - Workgroup 3
Chairs: S. Voss - TU Bergakademie Freiberg and T. Kasper - Univ. Duisburg

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K. Moshammer[1], R.X. Fernandes[1]

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SMARTCATs 2nd General Meeting - Workgroup 4
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PCA & Kriging For Surrogate Models

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N. A. Slavinskaya[1], A. Mirzayeva[1], W. Li[1], M. Frenklach[2]

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An Open Science Cloud for Molecular Science Services

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ChemConnect2016: Interconnected Network of Combustion Data

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SMARTCATs 2nd General Meeting - Poster session

Methane Oxidation over Doped Nickel Catalysts under Reforming Conditions: A DFT Study

I. Papadimitriou, G. Skevis, A.G. Konstandopoulos

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I. Naydenova, A. Filipov, Ts. Petrova

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K. Souflas, G. Paterakis, E. Dogkas, P. Koutmos

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SMARTCATs 2nd General Meeting - Poster session

Reduction and Optimization of Reaction Mechanisms for Hydrogen and Methane Combustion with Iron Compounds

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The Impact of Calcium and Potassium on the Pyrolysis and Combustion of Biomass

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Operating Parameters Adjustment of a Diesel Engine Running with Hydrotreated Vegetable Oil

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Insights on Complex Carbonaceous Material Structure by Mass Spectrometric Tools

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Combustion of Turkish Lignites and Olive Residue:Experiments and Kinetic Modelling

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ABSTRACT FOR SMARTCAT 2016

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Empiric and kinetic model advances of industrial applications of heating and diesel fuels.

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Ambient air quality has been largely improved during the last decades and it is expected to continue on this way. European Directive 2008/50/EC is devoted to the quality of ambient air and to have a cleaner atmosphere. Up to now, the attention of the European Commission has been focused on particulate matter and nitrogen dioxide.   The high concentration of heating boilers and light duty vehicles in cities requires a proper monitoring in order to assure the highest improvement on air quality.

Experimental and field data are the best source of data but modeling is a very useful tool to reduce the cost and duration of experimentation plans and quality surveys. Additionally, modeling allows us to build projections of emissions with the time. Nevertheless, modeling capacity is limited; an empirical model is enough sometimes but in other cases a kinetic model is required.

This paper will explain the usefulness of an empirical model of NOx emissions of heating fuel when it is used on the latest technology boilers (condensation, blue flame). This model allows us to define the specifications of heating fuel in order to obtain NOx emissions on a similar level to natural gas.

The advances on the kinetic modeling of industrial applications will be commented, considering the use of heating fuels in advanced boilers and also the use of diesel fuel in Euro 6 engines. The necessary approach of the work in these fields is detailed an opportunity for collaboration is identified.

Similarly, evaporation of fuel has a great impact on the quality of combustion. It is a very important factor for the temperature of combustion and the related emissions, no matter if we consider an internal combustion engine or a heating boiler. Additionally, the use of evaporation systems for low power injectors is a technology for boilers with high potential.   Therefore some effort has been dedicated to this topic and the main work areas will be shared in this paper.

Gas Turbine Fuel Flexibility

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Abstract

Combustion systems for current gas turbines are mainly designed for natural gas or oil distillates (typical class N.2) that are in some way standardized in terms of composition and thermo-physical properties. Nevertheless, it is more and more required from the market a certain flexibility of the gas turbine in terms of both the fuel variability during the operation and applicability of fuels completely different from standard ones; for example natural gas could exhibit significant variation of C2H6 or N2 content depending from the reservoir age or process economy (convenience of C2 removal), distillates could be heavier or lighter depending from the economical trade-off in that specific country, or the syngas produced by a specific gasification plant becomes more profitable if burned in a gas turbine.

Performances of the combustion system are strongly dependent on the fuel quality and properties; the behavior of the system may become unacceptable when some limits are exceeded. The sensitivity of the combustion system to the fuel is greater for the Dry Low Emission combustor (premixed flames) than for the traditional diffusive flame combustor.

A development program of Fuel Flexibility could be approached in two different ways:

1.   Given a certain combustor (designed and validated for standard fuels), it is required to verify operating and maintenance limits of the combustor related to the variation of fuel composition out of the standard intervals. The outcomes of this verification will be an eventual extension of such intervals around the standard ones and, in addition, the identification of combustor failure modes.

2.   Given a certain requirement of gas turbine performances (for example power range, efficiency, NOx emission) for a certain "non-standard" fuel, it is required to design and validate a combustion technology that allows satisfying the request. This second way provides a broad set of scenarios: traditional combustor could be already suitable and verified in the new fuel interval, or minor design modifications are necessary, or it is necessary to develop a new combustion technology to overcome some operating limit.

Aim of the presentation is to introduce the general problem of Fuel Flexibility, to illustrate the main current technical challenge in terms of analytical studies, experimental validations and product industrialization; finally, Ge O&G experience is briefly presented.

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Ignition delay time is not enough: modeling engine knock in gas engines

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Introduction and method

The globalization of the gas supply and the desire to incorporate renewable fuels into the energy supply are changing the composition of natural gas being supplied to end users. Thus, the hydrocarbon mix in natural gases is changing, and renewable fuels, such as hydrogen from excess renewable power ('power-to-gas') are being added to pipeline natural gas. A parallel development is the use of liquefied natural gas (LNG) as a land and sea transportation fuel, intended as a less polluting alternative for fuels such as diesel and heavy fuel oil. As is well known, engine knock in gas-fuelled engines is very sensitive to the fuel composition, and the occurrence of knock must be avoided: diminished performance, engine shutdown and even physical damage can result from knock. To define the limits of fuel composition guaranteeing knock-free performance for engine owners, it is essential to be able to predict the impact of composition on knock, accurately.

To characterize the effects of changes in the composition of gaseous fuels on engine knock the autoignition process during the compression and burn periods of the engine cycle must be analyzed and predicted. While the correct prediction of autoignition behavior of fuel mixtures is a clear prerequisite for predicting knock, it is furthermore essential to account for the effects of fuel composition on the in-cylinder pressure and temperature history relevant for knocking. These are caused by changes in heat capacity of the air-fuel mixture and in the phasing of the combustion process. Here, we present modeling results using a method that incorporates changes in thermophysical properties, combustion phasing and autoignition [1], which uses detailed chemistry to predict autoignition and a two-zone model to predict combustion phasing, and compare the results with those of experiments performed on a lean-burn, high-speed medium-BMEP gas engine. After a brief description of the computational method, the predicted and measured non-knocking pressure profiles are compared to indicate the importance of burning velocity in the predicted burn rates, while the comparison of the predicted ranking of knock resistance of fuels with measured Knock-Limited Spark Timing (KLST) exemplifies the necessity of accurate high-pressure autoignition mechanisms and faithful trends in burning velocities. The results are used to illustrate the differences in impact of changes in the composition of the fuel or fuel-air mixture on engine knock. Specifically, the effects of hydrogen addition to natural gas and the humidity of combustion air on engine knock are discussed.

Results

The modeling results for the pressure traces, verified with the engine experiments, show the strong increase in peak pressure caused by the increase in burning velocity with hydrogen addition, shifting the burn rate towards earlier times in the burn cycle with

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respect to top dead center. Together with the decrease in heat capacity upon hydrogen addition, this results in a strong increase in peak temperature in the unburned fuel-air mixture, up to 35 K for 20% H_2 in the mixture [2], which in turn clearly accelerates the autoignition chemistry towards causing knock. Under the in-cylinder conditions of the engine studied (peak T~1010 K, P=75 Bar and λ=1.5), H_2 admixture itself has only a modest effect on the autoignition delay time, leaving the impact on combustion phasing as the dominant effect. This effect of the increase in peak temperature with progressive admixture of H_2 on the predicted changes in engine knock is shown to be quantitatively in agreement with the measured changes in KLST [1].

The humidity of combustion air is known to impact the knock tendency of a given engine [3], with high humidity having a substantial knock-mitigating effect. Computed autoignition delay times [4] show only a marginal effect of water vapor on the ignition properties of methane and methane-propane mixtures up to 20 gH_2O/kg dry air. The measured non-knocking pressure profiles up to >75% relative humidity (11 gH_2O/kg dry air, at the temperature used) clearly reflect the impact on the combustion phasing. Modeling these profiles [4] exposed the impact of both the reduction of burning velocity and increase in heat capacity with the increase in humidity on reducing the peak pressure and temperature during the burn cycle. Here too, the predicted effect of variations in humidity on engine knock is shown to reproduce the measured trends accurately.

The results presented reflect the importance of accurate methods to predict both autoignition chemistry and burning velocities under the conditions extant in gas engines.

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Development of flameless combustor for an inverted Brayton cycle microturbine used in residential microCHP

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In 2013, U.S. central-station power plants consumed 38.2 quads of primary energy to generate 12.4 quads of electricity with an average electricity generation efficiency of 33% when aggregated over all primary energy sources, including coal, natural gas, nuclear, hydro, and wind [1]. In the process, 67% of the primary energy was wasted as heat (25.8 quads) and about 2 billion metric tons of CO2 were emitted to the environment, which is about 38% of the total annual U.S. CO2 emissions [2]. Distributed CHP systems are an alternative to central-station power plants. In these systems, an electrical generation system located in a residence or at a commercial site consumes natural gas to generate electricity locally and then the exhaust heat is utilized for local heating needs (in contrast to being wasted at central-stations). The combined efficiency of primary energy usage in CHP can be higher than 80%. Since about 75% of the electricity generated from all central-station power plants is consumed by the residential and commercial sectors, CHP in these sectors can have a huge impact on both energy savings and CO_2 emissions reduction. In addition, CHP can bring power resilience to households and commercial entities to counter weather-related outages that cause billions of dollars of losses to the economy annually. [3]

Recognizing this business potential, MITIS started in 2013 the development of a residential microCHP system based on a micro gas turbine. Compared to competitive technologies (ORC, Stirling, ICE, fuel cells), a micro gas turbine can provide significant advantages such as high efficiency, multi-fuel combustion, simplicity and low maintenance cost among others. It is well recognized that to enable of a significant market uptake of this technology, the system should be sized accordingly to the residential demand (1-kWe output), produce a reduced amount of heat, provide a low CAPEX and a low maintenance cost.

The presentation will report on the progress in the development a flameless combustor for the micro gas turbine. Aside global reduction of CO_2 emissions due decentralization, it is very important to drastically control the emission of gases such as NO_x which are responsible for major health issues in the world. MILD or flameless combustion [4-6] is a combustion mode able to provide high combustion efficiency with very low pollutant emissions, even with high air preheating. In addition to the improved energy efficiency associated to the heat recovery process, MILD combustion also ensures a homogeneous combustion environment, as a consequence of the intense recirculation of exhaust gases. This results in a localized reduction of O2 level, leading to a distributed reaction zone and reduced working temperatures with respect to conventional flames. The reduced temperature levels and the homogeneous reacting environment have a positive effect on both the formation of pollutants (NO_x, soot), which are substantially reduced, and the resistance of materials, thanks to the absence of sharp temperature gradients.

MITIS has designed a flameless combustor suited for the large λ required by the cycle of the micro gas turbine. The combustor consists in a main combustion and secondary mixing zones. Due to the special geometry of the combustor and design of the gas injectors, a major

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recirculation of the combustion products is achieved which dilutes the oxygen content of the inlet air in order to reach good conditions for the flameless combustion regime to occur. The new combustor has been modelled in detailed with advanced CFD analysis. The methodology is based on the resolution of the axisymmetric Navier-Stokes equations with k-ε turbulence model, the interaction of the combustion and turbulence is achieved through the Eddy Dissipation Concept model with reduced or detailed chemical reaction mechanisms. [7]

The presentation will report the results of two experimental test campaigns which demonstrate the very low NO_x emissions of the combustor for natural gas combustion at various inlet air temperatures and λ as shown on figure 1.
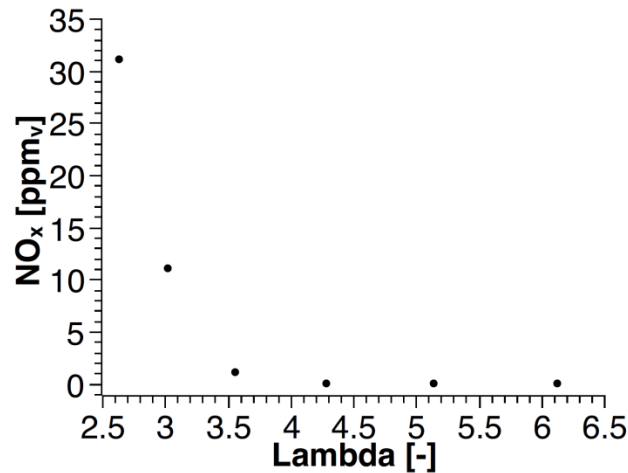
Figure 1: NOx evolution versus λ, air inlet temperature at 630°C

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"VADEMECOM: VAlidation driven DEvelopment of Modern and Efficient COMbustion technologies". An ERC granted project

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Combustion science will play a major role in the future quest for sustainable, secure and environmentally friendly energy sources. Two thirds of the world energy supply rely on combustion of fossil and alternative fuels, and all scenarios forecast an increasing absolute energy supply through combustion, with an increasing share of renewables. Thus, combustion will remain the major actor in transportation and power generation as well as in manufacturing processes, like steel and glass.

Nevertheless, combustion science will need profound innovation to meet future energy challenges, such as energy efficiency and fuel flexibility, and ensure future generations with affordable and sustainable energy and healthy environment. In this context, MILD combustion represents a very attractive solution for its fuel flexibility and capability to deliver very high combustion efficiency with virtually zero pollutant emissions. Such a combustion regime is the result of a very strong interaction between turbulent mixing and chemical kinetics. The fundamental mechanism of this interaction is not fully understood, thus justifying the need for experimental and numerical investigations.

The overall objective of the present research proposal is to drive the development of modern and efficient combustion technologies, by means of experimental, theoretical, and numerical simulation approaches. New-generation simulation tools for MILD combustion will be developed, to reduce the dependence on sub-grid models and increase the fidelity of numerical simulations. High-fidelity experimental data will be collected on quasi-industrial systems, to disclose the nature of the interactions between fluid dynamics, chemistry and pollutant formation processes in MILD combustion. Experiment and numerical simulations will be tied together by Validation and Uncertainty Quantification techniques, to allow the groundbreaking application of the developed approaches and promote innovation in the energy sector.

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A Steady State Model of Agricultural Waste Pyrolysis

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Abstract

Ever increasing energy demand and the climate change problem caused by anthropogenic greenhouse gas emissions have resulted in the worldwide effort to find a sustainable and environmentally friendly alternative to today's fossil fuel-dominated energy supply. There is potential for biomass waste (agricultural residues, forest residues and food processing waste) to be useful in solving some of the world's energy and environmental problems, as it is widely recognized as an environmentally friendly and renewable energy source.

Agricultural waste is one of the main renewable energy resources available especially in an agricultural country such as Serbia. It is estimated that every year in Serbia, a total amount of 4.24 million tons of agricultural residues is produced, which is equivalent approximately to 1.71 million tons of oil equivalent (toe).

Several thermochemical techniques, such as pyrolysis, gasification and combustion processes, have been proposed for biomass conversion into hydrocarbon fuels. Among these techniques, pyrolysis has already been considered as an attractive alternative for agricultural waste, since the technique can convert the special biomass resource into granular charcoal, non-condensable gases, and pyrolysis oils, which could furnish profitable energy and chemical products owing to their high calorific value. Compared with combustion, which is widely practiced commercially, and gasification, which is being extensively demonstrated around the world, pyrolysis of biomass is still at the stage of being developed for commercial use, and needs to overcome a number of technical and economic barriers to compete with traditional fossil fuel-based techniques [1], although numerous projects have been promoted. In this regard, the development of thermochemical processes requires a good understanding of pyrolysis mechanisms. This includes determination of the most significant pyrolysis parameters and their effect on the process, plus determination of the pyrolysis products (complex mixtures of the volatile matter and charcoal).

Regard to all mentioned above, based on experimental and literature data analysis pyrolysis of most available agricultural waste biomass), an analytical semi-empirical model was developed to provide a guide for the pyrolysis characteristics of biomass waste, to determine the yields of charcoal, tar and volatiles produced during biomass waste pyrolysis, and to determine the composition of the light gas (CO_2, CO, H_2 and CH_4) during conditions typically found in pyrolysis (300–950 °C). The literature analyses contained many experimental studies of biomass pyrolysis, regarding mechanisms, kinetics and product distribution. The experimental analysis included corn cob pyrolysis analysis, considering that corn cob, as an agricultural residue, has statistically high energy resource potential in Serbia (1.5 million tons of

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corn cob per year, or 0.7 million toe). This empirical model compiled the collected experimental and literature data in a structured tool that can be effectively used to analyze the biomass waste pyrolysis process [2-10]. The developed analytical semi-empirical was validated with open circles experimental data from other literature studies [11, 12]. The model validation show that prediction capability of the analytical semi-empirical model is in the good agreement with results obtained by literature review. The compact representation can be used in applications to conveniently extrapolate and interpolate these results to other temperatures and biomass types. Also, considering that pyrolysis is a key conversion stage during gasification and combustion, the proposed model can be implemented in biomass gasification and combustion mathematical models.

Keywords: agricultural wastes, corn cob, pyrolysis, products, steady state, modelling

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Uncertainty Quantification of chemical kinetics for MILD Combustion

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Introduction

With an increasing energy demand, and stricter regulations on emission from combustion processes, new and more efficient combustion technologies needs to be implemented. Moderate or Intense Low-oxygen Dilution (MILD) combustion is a technology which is becoming more and more popular. In MILD combustion the fuel stream is preheated and diluted by recirculating the hot flue gases. When the fuel has reached a temperature above self ignition temperature, MILD conditions has been reached. For these conditions there are no temperature peaks and the temperature is more homogeneous in the combustion chamber. This increases the combustion efficiency and reduces the NO_x emissions.
Due to the good mixing between the fuel and oxidizer in MILD combustion, the chemical time scale and the mixing time scale are in the same order of magnitude. The use of a detailed chemical mechanism is therefore necessary for simulations of this process. Existing detailed mechanisms have all been optimized and validated for conventional combustion, but the performance for MILD combustion is lacking. This work is therefore dedicated to quantifying and minimizing uncertainties in the chemical kinetics for MILD combustion.

Methodology

The test case used here is based on the work from Sabia et al. [1], where the ignition delay time was measured for a mixture of methane in a Plug Flow Reactor (PFR) at different inlet temperatures and for different *C/O* ratios. The stream was further diluted with nitrogen to reach a total nitrogen content of 85% in order to reach MILD conditions. The inlet velocity of the mixture was kept constant at 35m/s. To reproduce these results numerically, the software OpenSMOKE++ [2, 3] was used. Based on results from [4], where an evaluation of several detailed mechanisms for this specific case was performed, the POLIMI C1-C3 (Version1412, December 2014) [5] chemical mechanism for high and low tempertatures was used for the simulations. This mechanism consists of 107 species and 2642 reactions.
To determine which parameters that affects the simulation the most, an impact factor was used to rank the different reactions in the chemical kinetics. This impact factor is calculated by multiplying the sensitivity coefficients with the uncertainty factor for the corresponding reaction parameters. The sensitivity coefficients were calculated with respect to temperature at moment of ignition and the uncertainty factors were extracted from [6].

Results

Based on the impact analysis of the chemical mechanism, the formost reactions was determined to be $HO_2 + CH_3 = OH + CH_3O$. For this particular reaction the only value given is that of the Arrhenius parameter. This introduces a big uncertainty to the reaction rate, which is why the impact factor is so large. A surrogate model was then created based on samples from a standard Design Of Experiments (DOE), and used for the evaluation. For an experimental uncertainty of 10%, consistency for different C/O ratios was reached, but global consistency was not found. In Figure 1 the comparison between the standard kinetics, a prior uncertainty range and a new uncertainty range where consistency for all the measurement was reached, can be seen in a so called Arrhenius plot for one C/O ratio.
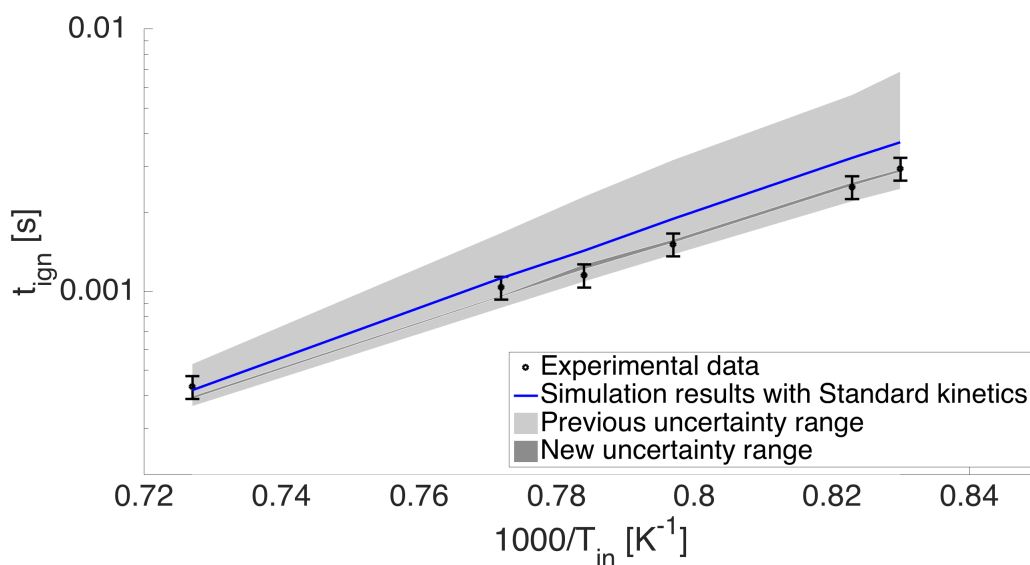
Figure 1: Ignition delay time at different inlet temperatures at $C/O = 0.025$.

Conclusion

By using UQ on chemical kinetics, the uncertainties in chemical mechanisms can be reduced and the accuracy of the simulations of MILD combustion can be improved. But it can also be determined from this work that including only one reaction in the UQ process is not enough to reach global consistency for the case presented here. The amount of reactions will therefore be increased in future work.

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DESIGN AND DEMONSTRATION OF A GAS-SOLID VOR-TEX REACTOR FOR THE FAST PYROLYSIS OF LIGNO-CELLULOSIC BIOMASS

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Fast pyrolysis of lignocellulosic biomass is regarded as one of key potential technologies for the production of chemicals, fuels and energy. Ideally, fast pyrolysis is carried out at conditions that allow high interfacial heat transfer, precise temperature control and short residence times of the pyrolysis vapors (<< 1 s). The latter implies also rapid cooling of the pyrolysis vapors and efficient removal of char.[1] Several reactor configurations have been developed during the last decades, and technologies were scaled up to demonstration and industrial plant scale: static and circulating fluidized beds, rotating cone, ablative and auger reactors. With the currently established reactor technologies it has not been possible to reconcile the actual and required operation conditions, particularly the accurate control of the reaction temperature and the minimization of the residence time of the pyrolysis vapors. Here we present the design of a demonstration unit for fast pyrolysis based on a novel reactor technology which address those issues by carrying out fast pyrolysis in a centrifugal field. By establishing centrifugal forces that exceed gravity multiple times a dense and uniform bed of particles can be formed, in which gas-solid slip velocities are three-to-five times those of conventional fluidized beds.[2] Larger gas-solid slip velocities leads to the intensification of interfacial transfer of mass, energy and momentum and to the reduction of the gas-to-solid space time ratio.
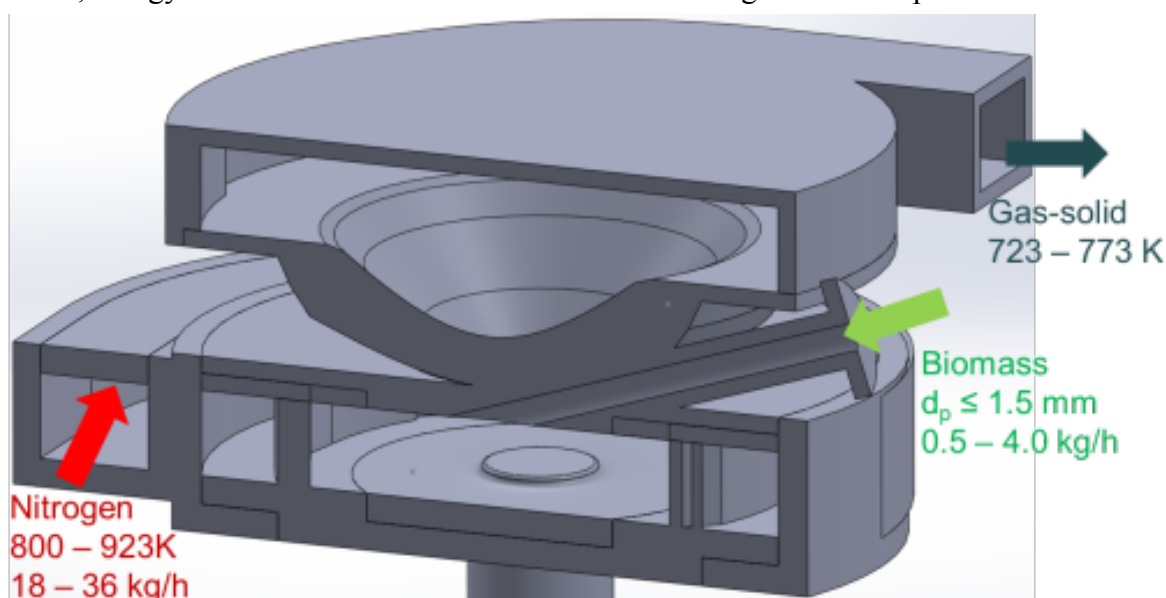

Figure 1. Gas-Solid Vortex Reactor schematics

The entire setup can be divided in five sections: Gas-Solid Vortex Reactor (GSVR), solids feeding, carrier gas conditioning, char separation and bio-oil condensation. The center piece of the demonstration unit is the GSVR, which consists of two concentric cylinders. As can be

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seen in Figure 1 the carrier gas is distributed around the annulus and enters the inner cylinder via eight rectangular inlet slots of 1 mm width positioned at a 10° angle with respect to the tangent. Biomass is fed into the inner cylinder, next to the inner wall, via a circular conduit of 10 mm diameter positioned at an 18° angle with respect to the horizontal plane. The axial length of the reactor is 15 mm and the diameter of the inner chamber is 80 mm. Momentum is transferred from the gas to the particles, causing them to rotate in the chamber and generating a large centrifugal force. Mass and energy balances on the GSVR showed that the biomass mass flow rates, which can be processed, range from 1.4×10^{-4} to 1.4×10^{-3} kg s-1. The corresponding gas (N_2) mass flow rates and inlet temperatures are 5.0×10^{-3}-1.0×10^{-2} kg s-1 and 800-923 K. At the aforementioned operation conditions, heat transfer coefficients of 350-450 W $m^{-2}K^{-1}$, i.e., three to five times those of conventional fluidized beds, can be reached.[2] A mathematical model of the reactor, which incorporates intra-pellet heat transfer, was developed and used to assess the effects of solids and gas flow rates, moisture content and pellet size on the yields of bio-oil, gas and char.

The solids feeding section consists of a combination of a gravimetric feeder, equipped with twin screws, and an "in-house" developed injector screw. The carrier gas conditioning section consists of a 100 kg liquid N_2 dewar, which is connected to an electric vaporizer and two packed bed heat exchangers. The heat exchangers are connected in series and they are indirectly heated by electric heating modules. Downstream of the GSVR, char is separated by means of a high throughput cyclone connected in series with a high efficiency cyclone. The pyrolysis vapors enter tangentially into a double tube heat exchanger integrated with an electrostatic precipitator. The heat exchanger is folded in a double U form which allows collecting two fractions of bio-oil. Cold flow and reactive Computational Fluid Dynamic (CFD) studies[2] have shown the suitability of the GSVR for biomass fast pyrolysis. The first results obtained with this demonstration unit will be discussed, demonstrating the concept and illustrating its process intensification capabilities.

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Experimental investigation on emissions and stability of combustion processes with high level of internal recirculation for small-scale technologies

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Abstract

Gas recirculation has been used for a relatively long time to stabilize combustion processes in several practical systems. To this aim several configuration have been considered based on fluid-dynamic stabilization by swirling or other strongly convoluted flow fields, as well as on external and internal gas recirculation or regenerative systems, trapped vortex [1-4].

It represents a challenging strategy to stabilize the oxidation process for novel combustion processes that aim at reducing pollutants emission, controlling the system working temperature by diluting the fresh incoming charge, and keep high process efficiency. The mass and sensible enthalpy ratio of recycled exhausted gas represents a key parameter to promote and stabilize the oxidation process.

Of course, this issue is directly related to the main requirements that a combustion process has to satisfy, related to its efficiency in terms of low pollutant emission, energy saving and fuel flexibility. These constrains, imposed by the energy market fast changing requirements, give rise to the need of defining new and advanced solutions allowing to use, in the same unit, a broad range of energy carrying molecules (i.e. fuels), according to local and time market offer while preserving combustion efficiency and eco-sustainability.

It is well assessed that recirculating heat and/or combustion products can have beneficial effects not only on flame stability but also on pollutants production. More specifically, in the last years several combustion modes inherently based on a strong recirculation process have been proposed and some of them found their way to commercial use. Typical examples are MILD, HiTAC and other regenerative burners (FLOX) [5-9] but also high intensity combustion devices have been proposed that rely on quite similar concepts [10-12]. One of the main limitations to the large deployment of recirculation based combustion devices is the difficulty in stabilizing small-scale systems due to the high heat losses.

Previous considerations poses the problem of identifying suitable configuration and geometries capable of realizing stable, efficient and clean combustion processes on small scale preserving the fuel flexibility needed and a reasonable degree of simplicity.

In this study we considered a configuration that can be considered ancillary both for the study of recirculation systems and recirculation zone in a full-scale system as well as small-scale burner configuration. Following, experimental tests were realized in a small size burner characterized by a strong internal recirculation ratio, induced by a cyclonic fluid-dynamic pattern obtained by the geometrical configuration of the reactor and of the feeding system (Fig. 1). The facility was designed to independently vary the mixture pre-heating temperatures and the mixture dilution levels [13, 14].

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In this context the combustion performances and stability of the cyclonic burner are analyzed to point out advantages and possible drawbacks of the burner as well as suitable working conditions and performances. Results suggest that the cyclonic configuration represents a challenging choice to stabilize the oxidation process while containing the pollutants emission for a large range of preheating temperature - mixture dilution levels extending the burner operability conditions with respect to the ones expectable on the basis of chemical/thermodynamic features of the process.
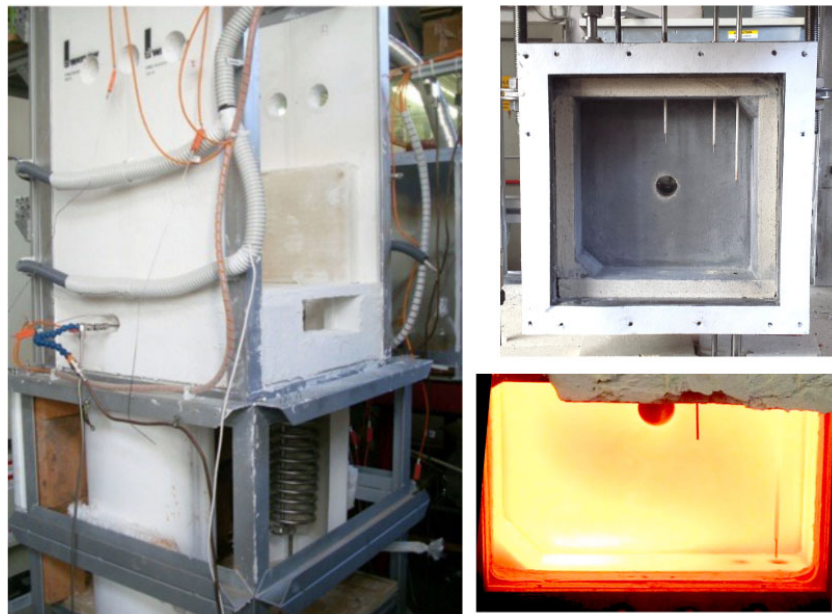
Figure 1   Pictures of the cyclonic combustion chamber in reactive conditions

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Analysis of a 20 kW flameless furnace fired by natural gas

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MILD combustion (Moderate or Intense Low-Oxygen Combustion) [1], known as Flameless Oxidation, is a combustion mode that allows to attain low NOx emissions, stable working conditions and significant energy saving by high air preheating. The technology needs the reactants to be preheated above their self-ignition temperature and enough inert combustion products to be entrained in the reaction region, in order to dilute both reactants and flame. The system is characterized by a more uniform temperature field than in traditional non-premixed combustion, and by the absence of high temperature peaks, thus reducing NOx and CO formation. This combustion technique is particularly interesting for low LHV fuels, such as biogas, coke oven gas (COG), syngas, allowing fuel flexibility and keeping a stable combustion.

Experimental facility and tests

This work focuses on the investigation of natural gas combustion in a 20 kW nominal power flameless unit, with integrated metallic finned heat exchanger to extract energy from the hot gases to pre-heat the combustion air. The unit is able to reproduce some of the main features of industrial furnaces (different injection profiles, air excess, fuel and air velocity, variable load). The chamber is made of stainless steel and equipped with a ceramic fiber insulation layer of 20 cm on the four sides. It has a cubic internal section of 0.75 m on each side. The air and fuel injectors are coaxial and placed on the bottom side, as well as the exhaust outlet. Therefore, the inverse flow configuration allows the combustion products to recirculate and dilute the reactants before combustion takes place. The combustion chamber is equipped with an air cooling system immersed inside it. Varying its mass flow, it allows the combustion chamber to operate at different stable conditions, to simulate the effect of a load. On each side of the combustion chamber, an opening is available for measurements. It can be equipped with a quartz window allowing optical access to the chamber for OH* chemiluminescence imaging, or it can accommodate thermocouples to measure wall temperature profiles. In the first case, the window can be fixed in the upper or in the lower side of the slot, allowing a complete access to the reactive zone.

A full characterization of natural gas flameless combustion is foreseen in the present work, varying different parameters, such as the power input (10-25 kW), the furnace set-point temperature (900-1000°C), and air excess (10%-20%). Experimental results include wall temperatures (on two sides), power balances, combustion efficiency, flue gas analysis (CO, NOx, O_2, CO_2, CH_4), and OH* images of the combustion zone. The latter is of paramount importance to detect the reactive region extension and shape.

Figure 1 provides the typical evolution of NOx emission versus time in the flue gases (test at input power 24 kW, Tset-point 950 °C and 15% air excess), highlighting the sudden drop, up to few ppm, associated to the switch from flame to flameless operation.

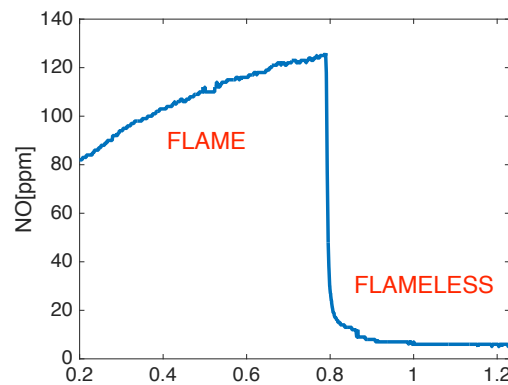*corresponding author*: M. Ferrarotti marco.ferrarotti@ulb.ac.be

Figure 1: Time evolution of exhaust gases NOx concentration. The sudden drop of NOx concentration is associated to the switch from flame to flameless operation

Numerical Analyses

The numerical modeling plays an important role to predict the behavior of flameless combustion, allowing to understand better the ignition process and the reactive propagation. This will guarantee a guideline to perform the experimental campaigns adopting LHV fuels, where the injection velocity and reaction region shape are different compared to NG. The mathematical modeling has been carried out with the commercial software ICEM CFD and FLUENT, both owned by Ansys Inc. Due to the presence of axi-symmetric planes, only a geometry sector of 90° has been considered. The computational domain consists of three sub-domains: the head of the burner and the combustion chamber. Two different approaches have been adopted for the generation of the computational grid. Three different grids (700k-1.5M -3M cells) have been generated and a grid convergence analysis has been carried out to choose the optimal mesh resolution. The selected grid consists of around 1.5M cells and contains parts meshed with tetras (head of the burner) and parts meshed with hexahedrons (combustion chamber). Specifically, there are 150k tetras and 1350k hexahedrons. The choice of a hybrid grid is justified to reduce the number of cells required to define the computational domain accurately and due to the complexity of meshing the first zone. The mesh independency analysis has been conducted using methane instead of natural gas, keeping the same input power, in order to use a simplified combustion model, such as the Eddy Dissipation Model/Finite Rate Chemistry (ED/FR) and accelerate convergence. Afterwards, the selected grid has been object of further investigation, keeping the same flow rates setting, but adopting the actual natural gas composition, more accurate combustion model (EDC) and detailed kinetic mechanisms (i.e. GRI 3.0 [2]).

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Woody residues torrefied and pelletized at the small scale: a new energy carrier as a replacement for fossil fuels

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Introduction

The paper presents an innovative pilot plant aiming at the torrefaction of woody residues. The so-called "TORPLANT" project aims at upgrading various local sources of biomass residues in order to produce pellets, heat and electricity based on a concept developed by the HEIG-VD. The project received financial support from the Swiss state of Vaud within the framework of their program "100 million for renewable energy and energy efficiency".

Pilot plant description

The installation, shown on figure 1 (next page), has a nominal output capacity of 100 kg/h. It is designed to process locally produced biomass residues such as wood waste from logging, green waste from waste collection centers and waste from anaerobic digestion units that are currently not integrated into recovery chains. The plant can run in automatic mode with remote supervision in order to reduce the cost of production of the solid biomass fuel. The pellets produced from torrefied biomass have an energy density that is up to one third greater in comparison to classical wood pellets. This enables a reduction in the storage and delivery costs. In addition, the global energy requirement for the process is reduced due to the very effective recovery of energy from the gases produced during the process (Torgas).

Initial results

Economic calculations have shown that a commercial plant of small capacity (500 kg/h output) can achieve good profitability and a ROI of 2-3 years with the current cost of biomass residues in Switzerland.
The commissioning of the pilot plant took place in May 2016. The paper will present the results of test runs expected to continue until December 2016 and conducted during 4 days of 24h/24 operation. The tests activities include tests of different biomass raw materials and operating conditions and recording of all input, process, and output parameters thereby enabling the calculation of the energy efficiency of the various stages, in particular (not exhaustive):
- Raw Biomass supply with a conveyor belt
- Grinder to produce smaller size chips (< 30 mm)
- Tumbling dryer heated both by thermal oil and Torgas combustion gases
- Torrefactor
- Flox® burner and gas turbine/compressor system
- Thermal oil heat exchanger

In addition, the results of torrefied biomass physical-chemical caracterisation and of several combustion tests will be reported in order to evaluate the torrefied products as a substitute fuel for biomass chips and pellets.

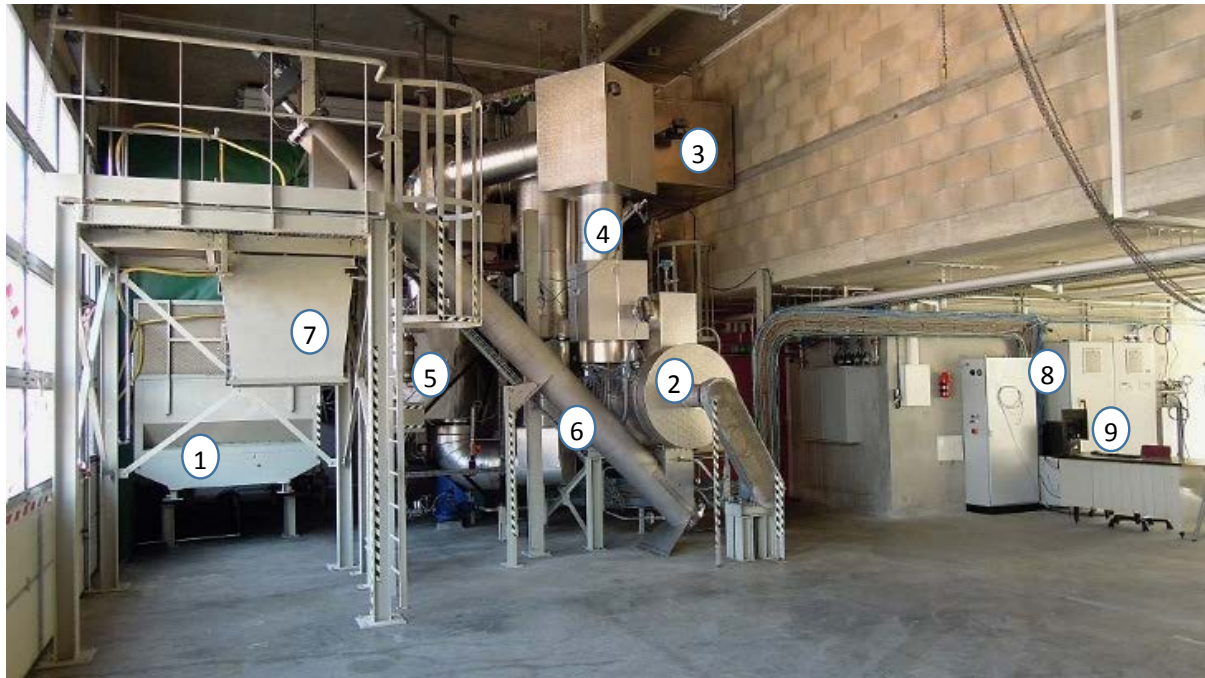*corresponding author*: Jean-Bernard Michel, jean-bernard.michel@heig-vd.ch

Figure 1 – Photograph of the pilot plant ©Granit Technologies SA

1.   Raw biomass storage and feeding system
2.   Torrefactor (biomass dryer not seen in the upper-back)
3.   Thermal oil heater
4.   Torgas line to the burner
5.   Flox burner system with A-Actor turbine and compressor
6.   Screw cooler of torrefied chips
7.   Output hopper
8.   Power supply and control cabinets
9.   PC Control & supervision

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Emissions and Performance of Diesel – NG Dual Fuel Engine Operated with Stoichiometric Mixture

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Introduction

Carbon dioxide emissions, particle matter and nitrogen oxides are the most important exhaust gas emission components from the compression ignition internal combustion engines. The Diesel cycle shows a superior thermal efficiency compared to the spark ignition (SI) combustion however the complete substitution of the Diesel fuel with natural gas is impossible for compression ignition (CI) engines. Partial substitution of Diesel fuel with less carbon fuel seems to be a meaningful approach to a step reduction of CO_2 emissions. As yet the majority of DF engines research and development activities were focused on large bore and heavy duty engines operating on lean mixtures, the works [1] and [2] indicate the possibility of exploitation of DF principle in the light duty engines operating in stoichiometric region.

The goals of this work are: 1) to explore a dual fuel natural gas Diesel operation for diesel engine of the cylinder size and structure compatible with engines for passenger cars and vans. 2) To identify the potentially interesting regions for practical use of the dual fuel natural gas Diesel combustion in a broad area of loads and NG substitution ratios from the pure Diesel combustion to the maximum achievable NG quantity. 3) To acquire the experimental dataset for validation of in-house developed diffusion combustion models. The acquired data will also serve as a base line for future investigations of advanced low temperature combustion modes for further reduction of PM and NOx emissions.

Experimental Setup

The experiments were conducted on an AVL 5402 Diesel single cylinder research engine of bore/stroke 85/90 mm with compression ratio 16:1. The engine is equipped with a common rail Diesel injection with a centrally mounted injector. For a dual fuel operation a CNG port fuel injector was installed in the intake manifold. A rapid prototyping engine control unit (ECU) was used for an independent injection control of both fuels. An in-house developed control algorithm built in Matlab/Simulink was used for a complete control of fuel diesel rail pressure and a precise control of multiple injections per cycle for both Diesel and gaseous fuel.

Visible smoke level was sensed using filter smoke meter, opacimeter and particle counter simultaneously. All gaseous emissions were measured in the raw exhaust gas. Molar fraction of nitrogen oxides was determined using chemical luminescence detector method, total hydrocarbons and methane emissions via flame ionization detector (FID), and carbon monoxide and carbon dioxide (CO_2) via non-dispersive infrared (NDIR) measurement technique. Content of oxygen was measured by a paramagnetic detector.

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In-cylinder pressure, instantaneous injectors control currents were sensed by a high speed data acquisition system. The tests were carried out at at constant speed of 1500 rpm using standard pump quality Diesel and grid natural gas.

Results and Conclusions

It was concluded that lambda = 1 operation at full load enables to increase the power output compared to pure Diesel operation without soot penalty. At low load and high NG substitution ratios the combustion efficiency steeply drops and the dual fuel operation is not feasible. The DF operation shows lower indicated efficiency than the Diesel one mainly due to incomplete combustion of methane. It was observed that the NOx emission increases as the Diesel diffusion combustion is replaced with premixed DF combustion. The PM and soot emissions of DF combustion are significantly lower at all loads than for the pure Diesel combustion.

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Acknowledgments

Combustion and emission analyses of tire pyrolysis oil in a common rail Diesel engine

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Introduction and Scope

Tire pyrolysis oil (TPO) represents a promising waste-derived fuel for Diesel engines with its main deficiency being lower cetane number compared to the Diesel fuel (D2). Recently, our group demonstrated for the first time the successful combustion of the pure TPO without the use of cetane improvers and any external energy addition in a turbocharged multi-cylinder Diesel engine [1], where a Diesel fuel like operation was demonstrated at higher engine loads without the use of an intercooler.

Presented research is taking this further by applying TPO tailored injection strategies and EGR rates to a state of the art 1.6L turbocharged and intercooled 4-cylinder common rail Diesel engine with the aim to further improve emission response, efficiency and part-load performance while utilizing pure TPO. This significantly facilitates its use and boosts its conversion efficiency to mechanical work. To achieve this objective an in depth analysis of the impact of different EGR ratios and different injection parameters on the combustion and emission formation phenomena of the pure TPO is performed. These results were benchmarked against the data obtained for the Diesel fuel. This holistic assessment provides guidelines and pinpoints suitable control strategies for efficient utilization of the TPO.

Furthermore, presented research provides, to the best of authors' knowledge, a foremost in-depth analysis of the particulate emissions of the TPO measured with different methods: the Micro Soot Sensor and the Gravimetric Filter Module. This analysis identifies and reasons challenges related to determination of the particulate emissions for alternative fuels like the TPO.

Results and Discussion

Presented research shows for a first time that a Diesel like combustion of pure TPO without the use of cetane improvers and any external energy addition can be achieved in a modern turbocharged and intercooled engine equipped with the common rail and the EGR. The influence of key engine control parameters that allow for achieving this objective can be summarized as:

- At least one pilot injection is needed for efficient combustion of pure TPO fuel in modern turbocharged and intercooled Diesel engine.
- Retarded pilot injection at unaltered main injection allow for achieving a Diesel-like combustion with pure TPO.
- Introduction of EGR helps to increase temperature at start of MI and by this reduces cycle-to-cycle variations to the level observed with D2.

It was also shown that with the use of TPO it is possible to achieve comparable gaseous emissions as those measured with the use of the D2. With variation of key engine control parameters, the following influences on TPO combustion were revealed:

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- Increasing EGR rate successfully contributes to reduction of NO_x emissions, while THC emissions increase, particularly at high EGR rates, low engine loads and high engine speed. The effect of EGR on CO emissions is marginal.
- Advancing main injection timing is steadily increasing NO_x emissions, which also reflect the effect of FBN, giving a steady rise over entire operating range of the engine in comparison to D2.
- Late main injection timing, particularly at low loads and high engine speeds is increasing THC emissions as a result of short combustion duration. In this case, CO emissions are marginally affected.

The influence of key engine control parameters on PM emissions was evaluated with two methods; MSS (measuring mainly soot with photoacoustic method) and MSS+GFM (measuring total particulates with gravimetric method). The findings can be summarized as follows:

- Soot emissions (measured with MSS) were two-fold higher than for D2. This reflects high PAH content of TPO.
- Introduction of EGR substantially contributed to soot emissions indicating the importance of sufficient in-cylinder oxygen concentration at the time of main injection.
- Large discrepancies were identified when comparing soot emissions (measured with MSS) to PM emissions (measured with MSS+GFM). Based on known composition of TPO, the reasons for discrepancy were identified to be different chemical composition, morphology and homogeneity of the PM of the TPO in comparison to the PM of D2 where MSS and MSS+GFM values coincided very well. These differences indicate that different environmental impact of the PM of the TPO is likely to be expected which suggests that a critical assessment of the PM effect on environment and health is necessary to impose plausible emission limits for alternative fuels.

The significance of this study can be recognized in elaborating the key guidelines on injection and EGR rate strategy that enable successful use of the pure TPO in modern turbocharged and intercooled Diesel engine over a very broad operating range, which makes it very interesting for example for the stationary power applications. Furthermore, this study opens challenges of PM emission measurement of alternative fuels with significantly different fuel properties compared to derivatives of the crude oil that go far beyond the presented analysis.

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Numerical and experimental study of a MILD combustor

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Demand for higher efficiency combustion systems lead to new technologies of energy systems and combustors. Today is fuel flexible combustors a growing trend and the different fuels are typically of LCV (Low Calorific Value), such as biofuels, syngas and landfill mixtures. The Swedish company Cleanergy has found a market niche towards renewable, gaseous mixtures that are relatively difficult to burn since the energy content is small compared to natural gas. The GasBox burner from Cleanergy is driving an α-type Stirling engine and the burner is designed to operate in the MILD (Moderate or Intense Low Oxygen Dilution) [1] combustion mode. The burner uses both air preheating and exhaust gas recirculation. The GasBox has been fitted in an atmospheric combustion test cell equipped with pressure sensors, a series of thermocouples and an advanced gas analysis system. In the experimental campaign, the main objective was to assess the effect of gas composition variation on the emissions (mainly NOx, CO and CO_2 and unburned hydrocarbons) and on the engine operation [2]. The effect of the engine pressure and the air-to-fuel ratio was also studied. During one operational cycle of the Stirling engine the lower heating value of the gas mixtures was decreased from 50 MJ/kg (100% CH_4) down to 6 MJ/Kg (~24% CH_4) using a fuel mixing equipment. In this wide range of mixtures, the combustion chamber has provided low emission values, Figure 1. The conclusion from the high qualitative data was that the engine performed well at all the conditions analyzed.
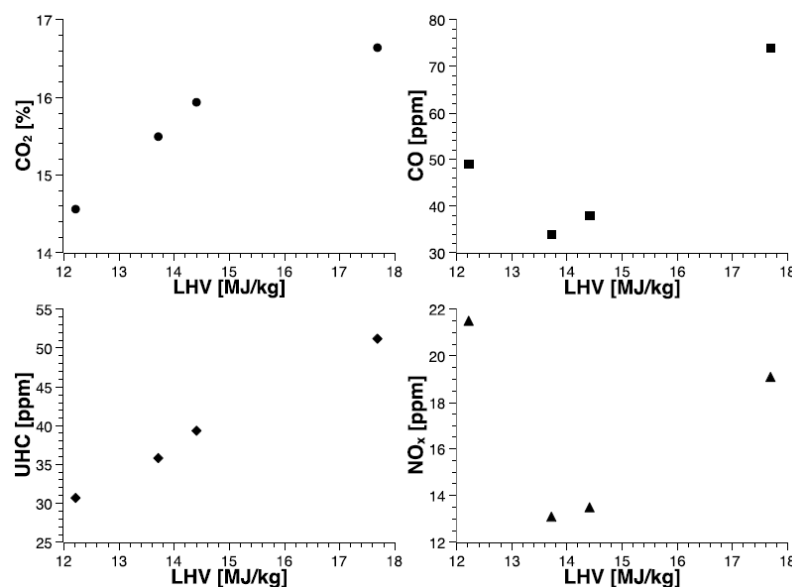
Figure 1. Emissions of the engine at 118 bar, [2].

CFD (Computational Fluid Dynamics) is an important tool for designing and optimizing combustion systems. RANS simulations have long been a very common approach for industrial simulation of reacting flows. However, the rapid increase in computer power in recent years has made feasible reacting flow simulations using more sophisticated turbulence models such as URANS/LES and LES [3]. One of the experimentally tested mixtures has been analyzed in a 3D CFD combustion simulations based on a RANS turbulence model using the commercial software Fluent. The simulation has radiative heat

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transfer included. The combustion is modelled using the eddy dissipation concept using the GriMech 2.11 reaction mechanism. The gas composition was consisting of 39.6% CH_4, 38.7% CO_2, 2.0% O_2 and 19.5% N_2 by volume. Specified mass flow rates was imposed at the inlet boundaries for the air inlet and the fuel inlet. The preheated air inlet temperature was set to 1000 K and to 300 K for the fuel inlet. The outlet boundary condition is set to 1 bar and a no-slip adiabatic boundary condition is imposed on all walls. The heat exchanger is included in the CFD simulations and is modeled by a heat sink in order to represent the amount of the heat that is extracted by the heat exchanger in the Stirling engine. Conservation checks were made for mass, momentum, energy and major species.

Figure 3 shows a contour plot of the temperature on a plane that is cut through the burner. The temperature distribution in the mixing tube is smooth and uniform. There is a good agreement between the quantities predicted and the experimental data, in terms of flow and flame dynamics, averaged temperatures and the concentrations of some major species.
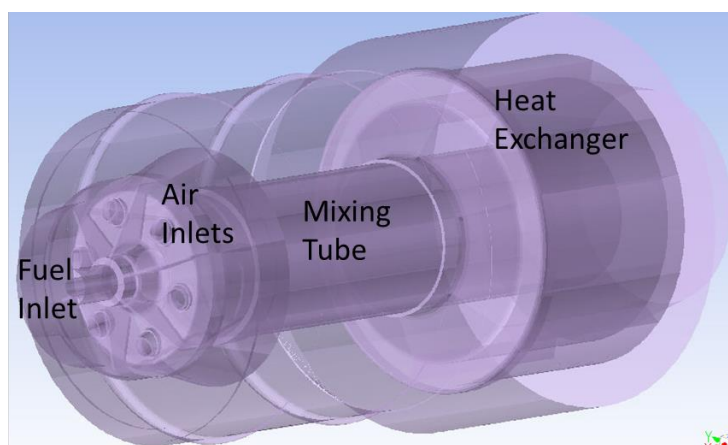
Figure 2. CFD-domain
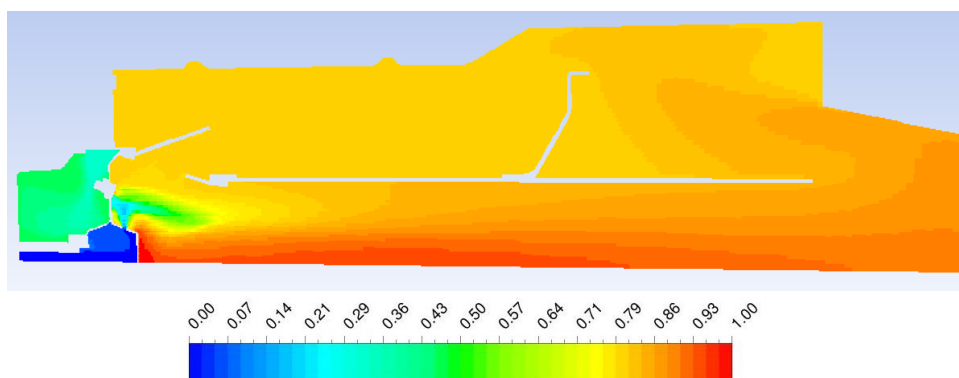
Figure 3. Static temperature: Steady-state CFD.

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Diesel injector cavitation and jet effects on the combustion chamber turbulence field

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The turbulence field promotes combustion and stabilizes flame in the combustion chamber environment of Diesel internal combustion engines. The injection process along with the design of cylinder head and piston contribute in the establishment of the combustible air/fuel mixture field. However, after the combustion initiation the flame and combustion processes development are further affected by the established turbulence field which enhances combustion stability. The main objective of the present work was to model the full three-dimensional Diesel injector flow and assess the effects of the cavitation phenomena within the nozzle on the pattern of the emerging liquid jet, on the resulting air/fuel mixture and the established turbulence field adjacent the nozzle exit. The computational domain of the symmetrical one sixth segment of valve-covered orifice sac-less six-hole Diesel injector was modelled and investigated for fully open needle, for injection in a quiescent constant volume chamber. An Eulerian approach was used incorporating the VOF model for the two phase flow and the Rayleigh model for the capturing of the cavitation phenomena. It was found that cavitation phenomena occur in the nozzles when the entry geometry is sharp, while cavitation phenomena are limited for nozzles with rounded entry geometry. It was observed that when cavitation is present there is asymmetry in the velocity profiles at nozzle exit, while air-fuel mixing and turbulence are more intense at the upper area of the jet, where cavitation preceded within the nozzle. From the present work simulations, it was found that a large scale recirculation zone is established at the upper area of the emerging spray jet, which causes high levels of turbulent kinetic energy for the case of injector flow wherein cavitation occurs. However, by increasing the injector nozzle length, then the turbulent viscosity magnitude decreases and the maximum values of turbulent viscosity are displaced at the lower area and towards the tip of the spray jet.
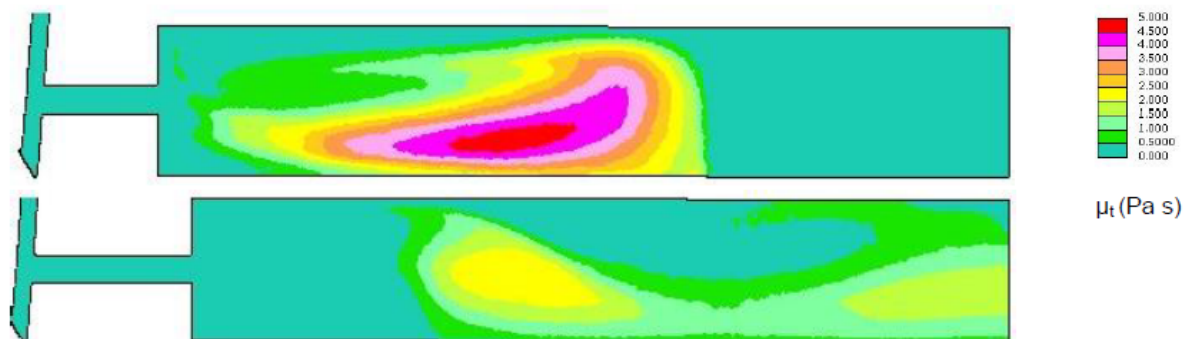

Figure 1: Predicted turbulent viscosity field in the constant volume chamber for a Diesel injector with short and long nozzle

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The reactions of atomic oxygen with unsaturated C4-hydrocarbons

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Because of their relevance in combustion, the rate coefficients for the reactions between ground state ^3P oxygen atoms and unsaturated hydrocarbons have been determined in kinetics experiments as a function of temperature. Much less is known, instead, on the chemical identity of the primary products and their branching ratios (BRs). This piece of information, however. is fundamental to build realistic combustion models, because the products of one elementary reaction become the reactants of a subsequent one in the intricate scheme of elementary reactions that account for the global combustion process [1]. For multichannel reactions like those of interest here, the primary products and their BR are not easy to predict because intersystem crossing (ISC) from the triplet to the underlying singlet potential energy surface (PES) can occur, opening up other reaction channels not accessible on the triplet PES. The quantification of ISC as a function of temperature is a demanding task.

For this reason, in our laboratory we have undertaken a systematic experimental investigation of this class of reactions by means of the crossed molecular beam technique [2] with mass spectrometric detection (CMB-MS). We remind that the CMB-MS technique permits one to (i) investigate bimolecular reactions under truly single-collision conditions, avoiding the complications of a multiple-collision environment and wall effects; (ii) verify unambiguously to which channel a given product belongs detected at a given m/z ratio; and (iii) assess the presence of potential energy barriers [1,2]. This experimental approach has been successful in the investigation of the reactions $O+C_2H_2$ (ethyne), $O+C_2H_4$ (ethene), $O+CH_3CCH$ (propyne), $O+CH_3CHCH_2$ (propene) and $O+CH_2CCH_2$ allene) [3-7].

In this contribution, new results on the reactions between atomic oxygen with two unsaturated C4-hydrocarbons, namely 1-butene and 1,2-butadiene, will be presented.

For the reaction O + 1-butene, we have experimental evidence that the channels leading to $H_2CO + C_3H_6$, $C_2H_5CHCO + H_2$, $C_3H_7 + HCO$, $CH_3 + CH_3CHCHO$, $C_2H_5 + CH_2CHO$, $C_2H_5 + CH_3CO$, and $C_2H_5CHCHO + H$ are open, as predicted by electronic structure calculations of the relevant potential energy surface [8]. The branching ratio at a collision energy of 10.4 kcal/mol has been determined.

For the reaction O + 1,2-butadiene, we have experimental evidence that the channels leading to H and H_2 elimination, as well as to the C-C bond breaking (with the formation of $CO + C_3H_6$, $HCO + C_3H_5$, $CH_3CO + C_2H_3$, $CH_2CHO + C_2H_3$, $CH_2CHO + C_2H_3$, $H_2CO + C_3H_4$, $C_3H_3O + CH_3$), are open [8] at a collision energy of 10.0 kcal/mol. Estimations of

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the product branching ratio as well as electronic structure calculations of the relevant triplet and singlet potential energy surfaces are currently under way.

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Formation of C_5 species from iso-butene.

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Iso-butene is an important intermediate for the oxidation and pyrolysis of branched alkanes such as iso-octane and that of octane enhancers such as MTBE (Methyl-tert-butyl-ether) and ETBE (Ethyl-ter-butyl-ether). The aim of this study is to extend the iso-butene chemistry, presented previously by Schenk et al. [1], including C_5 species like *n*-pentene, and cis-*2*-pentene.

The current model is a comprehensive mechanism that is able to describe the oxidation of hydrocarbon fuels from C_1 to C_4 based on a previous study [2] which represents butene and butane high temperature chemistry [1,3].

To evaluate the model, experimental measurements of premixed, laminar low-pressure flames (40mbar) for iso-butene have been used [1]. In the measurements C_5H_8 and C_5H_{10} species were detected where possible isomers for C_5H_{10} species are *2*-methyl-*1*-butene, *n*-pentene, and cis-*2*-pentene. The model presented in the work of Schenk et al. [1] focused on *2*-methyl-*1*-butene. In the new mechanism, high temperature reactions corresponding to *n*-pentene, and cis-*2*-pentene decomposition have been added, using corresponding reaction rates for high temperature following the rate rules presented in the work of Nawdiyal et al. [4]. Additional fulvene pathway suggested in the work of Nawdiyal et al.[4] and updates in the C_2 chemistry suggested in the work of Seidel et al. [5] are also included. As a result, a new reaction pathway that is giving more insight into the decomposition of iso-butene forming C_5 species is presented.
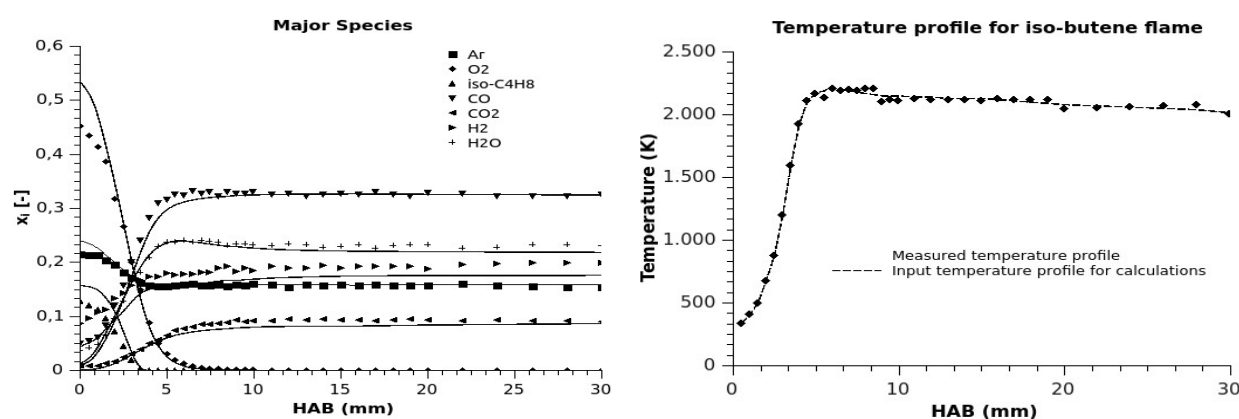

Figure 1. *Main species mole fraction (x_i) and disturbed temperature (T) profiles for the flames of iso-butene as a function of height above burner (h). Symbols represent the experimental data, lines represent the modeling results. Equilibrium values are indicated at 32 mm. Disturbed temperature profiles were obtained from the MBMS measurements, with NO-LIF calibration at 21.7 mm indicated in the insert table.*

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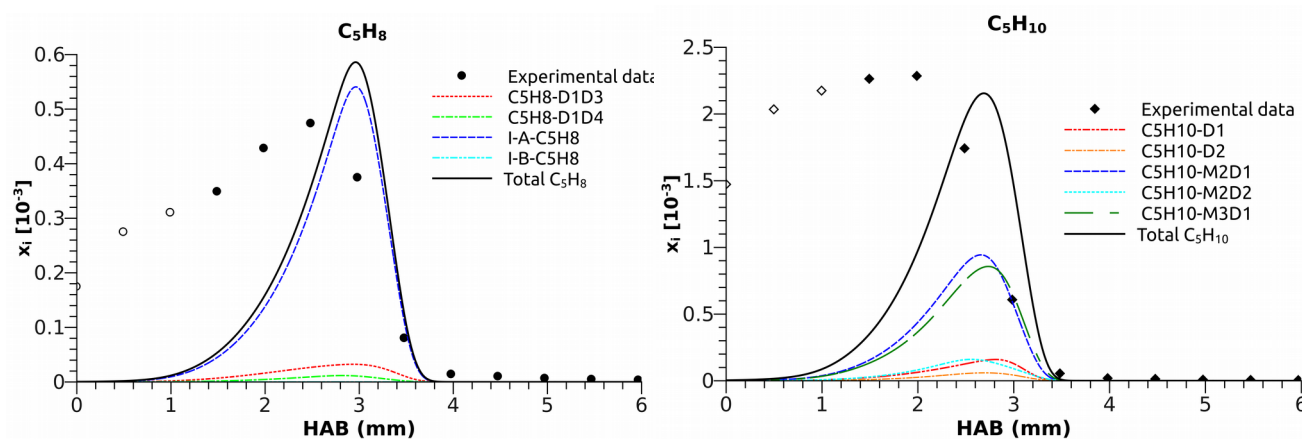
Measurements at h=1 mm (open symbols) may be affected by sampling probe effects.

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Unravelling the role of cyclopentadiene and hexadiene in the formation of aromatics

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The pyrolysis and oxidation of hydrocarbon and oxygenated molecules often leads to the formation of polycyclic aromatic hydrocarbons (PAH) which are considered the main precursors for deposits or soot particles [1]. Resonantly stabilized radicals, such as propargyl, allyl and cyclopentadienyl, have been identified as important intermediates for PAH formation [2, 3].
They have prolonged lifetimes compared to non-resonantly stabilized radicals and can therefore accumulate at fuel-rich oxidation or pyrolysis conditions. Recombination with other radicals in the reactive system is an important consumption route leading to molecular weight growth [4]. In this respect, the self-recombination of propargyl radicals to benzene has been investigated thoroughly [5]. Other important recombination channels routes that eventually lead to benzene include allyl plus propargyl and allyl plus allyl [4]. Self-recombination of allyl results in 1,5-hexadiene, which upon hydrogen abstraction from the allylic carbon atoms forms hexa-2,5-dien-1-yl. Cyclization of hexa-2,5-dien-1-yl produces C5 and C6 ring species [6]. Note that hexa-2,5-dien-1-yl is also formed by addition of vinyl on 1,3-butadiene [7]. The latter reaction channel has been recognized as a potential benzene formation channel [7].

On the one hand this study provides an experimental dataset regarding the oxidation and pyrolysis of 1,5-hexadiene, the self-recombination product of allyl, in a jet-stirred reactor. This is motivated by the interest to comprehend the role that 1,5-hexadiene and allylic radicals play in the formation of aromatics. Sixty products were detected and quantified in the reactor outlet gases. Mole fraction profiles of all species as function of reactor temperature are reported in supplemental material. A selection of mole fraction profiles are displayed in Figure 1 ($\varphi=\infty$).
In order to interpret the data, a kinetic model has been developed using an automatic network generation tool. This model was augmented with kinetic data from several recent literature-reported theoretical calculations. The model was used to simulate the obtained experimental data and to identify the main reaction pathways.

On the other hand novel pyrolysis data on the reaction of ethylene and 1,3-cyclopentadiene are discussed. The reaction paths that have been suggested in literature will be reevaluated and, various alternative pathways will be suggested. This study is further extended with theoretical work on the $C_5H_5 + C_2H_4$ surface. This –to our knowledge– unexplored surface plays an important role in the combustion and pyrolysis of many hydrocarbons that have ethylene and cyclopentadiene as their major decomposition products (such as JP-10, a widely used jet fuel). Calculations on this surface point to fulvene, cyclohexatriene, benzene and toluene as

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primary products. The results of these calculations will be validated with experimental data obtained in a bench scale reactor.
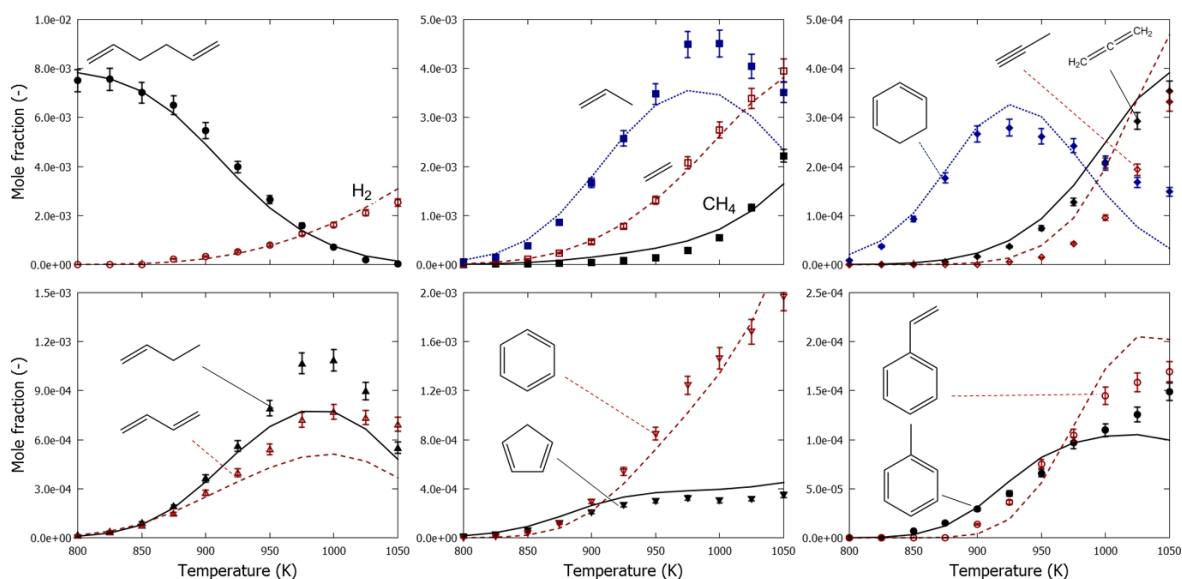

Figure 1: Mole fractions as function of temperature for 1,5-hexadiene pyrolysis in a jet-stirred reactor, P=0.107 MPa, F_V=4.06 10^{-5} m^3 s^{-1}, $x_{1,5\text{-hexadiene,0}}$=0.008. Symbols: experimental mole fraction profile of molecule represented in graph; Lines: simulated mole fraction profiles

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Experimental investigation of laminar hydrocarbon/hydrogen flames at elevated pressures

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Introduction

Energy production is heavily dependent on natural gas as a fuel and gas turbines are traditionally manufactured to achieve optimal operating conditions for natural gas with methane as the dominating combustible component. However, in recent years demands for fuel-flexible combustion systems have increased, as a result of increased use of industrial waste gases as fuels. The driving forces are related to economical as well as environmental aspects. By-products from industry can be heavier gaseous hydrocarbons like propane, but also the highly reactive hydrogen gas. These components can be mixed with natural gas, altering the fuel composition and thus the combustion properties of the mixture. Methane combustion is well understood, while studies on other hydrocarbon fuel components like ethane and propane have emerged the last few years. Co-firing with hydrogen promotes combustion, effects that have mainly been studied in methane/hydrogen/air flames [1].

The heavier alkanes ethane and propane are constituents of natural gas, as well as being industrial by-products suitable for combustion. They are slightly more reactive than methane and have been shown to burn with higher laminar burning velocities [2]. Experimental studies of mixtures of such hydrocarbons with methane are scarce, and no flame studies at all have been performed on hydrogen/methane mixtures with an additional higher hydrocarbon added. However, simulations reveal that the flame-enhancing effect of hydrogen can be dampened by the presence of ethane or propane [3, 4].

Recently a study on laminar flames stabilized on a heat flux burner at 1 atm confirmed that enhancement of laminar burning velocity is stronger for methane/hydrogen mixtures than for methane/hydrogen/ethane/propane mixtures [5]. Since real combustion applications involve operation at higher pressures the study is now continued by characterization of high-pressure flames. Here we report results from a study on premixed laminar Bunsen-type flames of methane/air and methane/ethane/air, with and without hydrogen addition.

This project is a work in progress and here we aim at presenting data on chemical species for flames of methane/ethane/hydrogen of various fuel composition.

Experimental details

Experiments were performed using a Bunsen-type burner enclosed in a high-pressure vessel, the setup has been described in detail by Joo et al. [6]. The vessel can operate at pressures up to 35 bar and premixed as well as diffusion flames of methane/air have been visited as test cases. Here we present data for premixed laminar flames at pressures up to 8 bar in a range of equivalence ratios from 0.9 to 1.3. At pressures up to 3 bar stable flames are achieved for this full range of equivalence ratios, while at pressures 4-8 bar rich flames with ϕ=1.3 were studied. The high-pressure vessel is designed to allow access for laser-diagnostic techniques such as laser-induced fluorescence for measurements of important species like formaldehyde, CH_2O, and the hydroxyl radical, OH. The main laser-diagnostic method in the present study is, however, Raman spectroscopy that enables simultaneous measurement of a range of species, giving a large dataset for characterization of the flames. In these studies the

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main aim is to monitor the stable species H_2, N_2, O_2, CO, CO_2, H_2O, and hydrocarbons. Figure 1 presents photos of flames of methane/ethane/air at equivalence ratio ϕ=1.3, pressures of 1, 4 and 8 atmospheres. The flame-cone is indicated by bright blue chemiluminescence from the CH-radical in the flame reaction-zone. A reduced laminar burning velocity at elevated pressures results in a higher elongated flame cone.
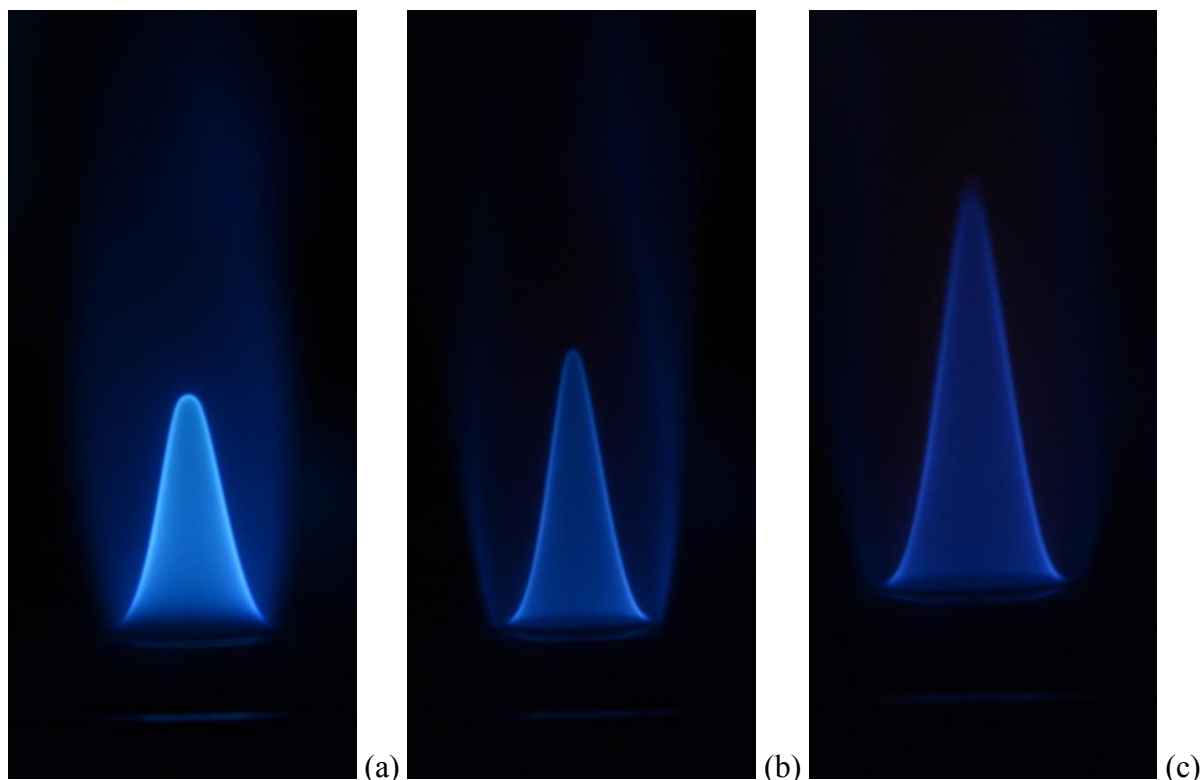

(a)   (b)   (c)

Figure 1. Flames of methane(80%)/ethane(20%) in air, at ϕ=1.3 and pressures a) 1 , b) 4 and c) 8 atm.

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Critical Issues of Chemical Kinetics in MILD

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Abstract

The control of system temperature enhancing the global heat capacity of the reactant mixtures by diluting the system with exhausted gases is becoming a common strategy in several combustion technologies, involving MILD-Oxyfuel processes for furnaces, boiler and turbines, or EGR and HCCI systems for engines, to minimize pollutants formation without renouncing to a high thermal and energetic efficiency.

Some problems rise when the chemical kinetic aspects are attempted to be modeled. The performance of kinetic schemes at high temperatures is insured by the proper description of the fast high temperature branching reactions of the sub-system H_2/O_2, supported by the availability of reliable and exhaustive experiments. They hide the elementary reaction constants uncertainties of slow reactions, reducing the impact of their relative weight in the prediction of combustion features. On the contrary, at low-intermediate temperatures, the oxidation processes comes through a larger number of species and slow elementary reactions whose uncertainties have a huge impact in the predictive performance of detailed models. In addition, the kinetic scheme validation procedure under these operating conditions suffers the lack of experimental results in simple facilities.

Under diluted conditions, the role of third molecular reactions in the oxidation chemistry at low-intermediate temperatures becomes crucial. Thus a proper description of the temperature and pressure dependence of third molecular reactions, along with the quantification of third body collisional efficiencies for H_2O and CO_2 becomes a crucial point for the predicting performances of kinetic models. Furthermore the "mixing rule" commonly employed in kinetic schemes have to be discussed when H_2O and CO_2 dilute the fresh reactants, because of the formation of complex interaction among species not responding to a linear rule.

In this perspective, a set of experiments realized in model reactors, namely a Jet Stirred Flow Reactor (JSFR) and a Tubular Flow Reactor (TFR), by changing the inlet temperatures, the equivalence ratios of the mixtures and the diluent species, are considered. The autoignition delay times and the oxidation regimes of CH_4/O_2 and C_3H_8/O_2 mixtures diluted in N_2, CO_2 and H_2O are reported [1, 2].

Under diluted conditions, the oxidation process occurs through several regimes. In particular temperature oscillations are detected during experiments in the JSFR reactor for both the considered fuels. This behavior is reflected in the data obtained in the TFR, where a NTC phenomenology is experimentally detected for both the simple hydrocarbons.

The numerical analyses suggested that such phenomenologies comes trough the competitions between oxidation and recombination/pyrolytic channels [3-4]. Under diluted conditions, the modest system working temperatures do not promote any dominating oxidation kinetic mechanism, thus oxidation pathway and recombination routes have comparable global reaction rates and interact in a complex-non linear manner in dependence of system operating conditions and heat exchange mechanisms to the surroundings.

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By considering the results obtained with mixtures highly diluted in N_2, the role of CO_2 and H_2O as "bath gas" is highlighted.

Fig. 1 shows the variation of the oxidation regimes identified for CH_4/O_2 mixtures diluted at 90% in N_2, in N_2 and H_2O with a relative steam concentration of 10% and 20%.
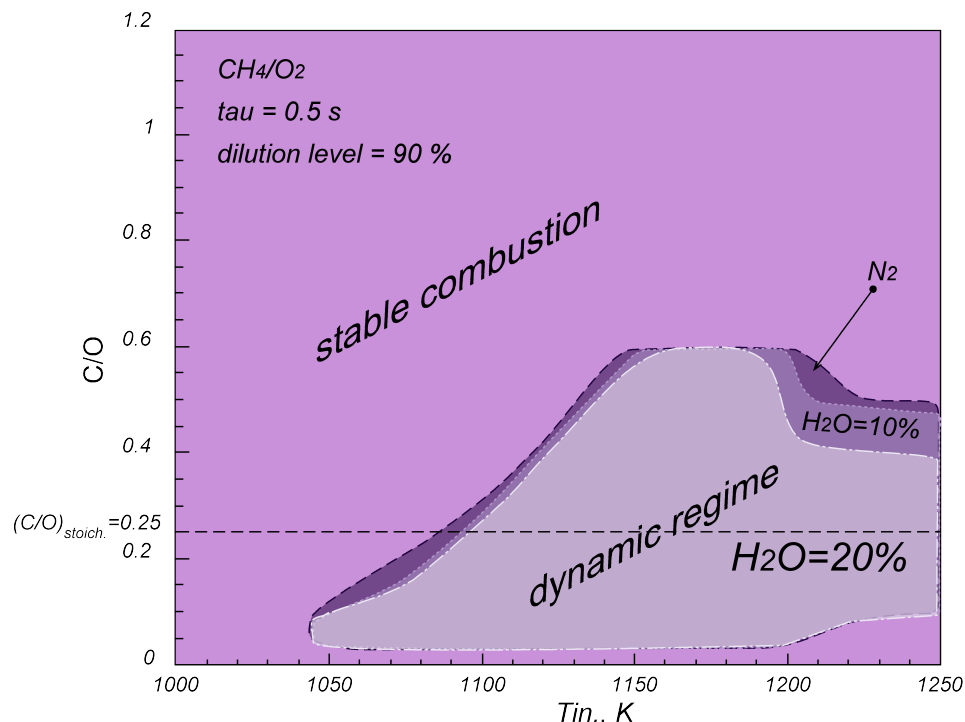

Fig. 1 Experimental behavior maps for CH_4/O_2 mixtures diluted at 90% in N_2 and mixtures of N_2 and H_2O (10 and 20%).

The papers aims at highlighting the model levels of criticality by discussing the performance of kinetic mechanisms in predicting such combustion phenomenologies coming out in model reactors for conventional fuels under low-intermediate temperatures, mimicking the operating conditions of diluted systems.

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Laminar burning velocity of diacetyl + air flames. Further assessment of combustion chemistry of ketene

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Ketene is important intermediate in high-temperature chemistry of several oxygenates, such as acetone, acetic acid, and diacetyl. Ketene reactions appear in the sensitivity spectra of calculated burning velocities of these species. To provide independent experimental data for validation of the ketene sub-mechanism, the laminar burning velocities of diacetyl + air flames at 1 atm and initial gas temperatures of 298 K, 318 K, and 338 K were determined for the first time. Measurements were performed using the heat flux method in non-stretched flames, stabilized on a perforated plate burner at adiabatic conditions. Recently developed detailed kinetic mechanism for acetic acid flames with updated ketene sub-mechanism has been extended by reactions of diacetyl and includes revised rate constants for reactions of acetaldehyde and acetyl radical. The model was first compared with available experimental data on ketene pyrolysis and oxidation. Its performance in prediction of C2 species formation was improved by significant reduction of the previously estimated rate constants of ketene reactions with CH_3 and CH_2 radicals. The updated mechanism was then compared with the new measurements for diacetyl and earlier data for acetaldehyde and acetone flames. The model closely reproduces burning velocity of diacetyl + air in lean and rich mixtures while underpredicts in stoichiometric and slightly rich flames. Performance of the model for acetaldehyde + air flames was much improved as compared to the Konnov mechanism version 0.6. Good agreement of the modelling with experimental data for acetone + air flames was also demonstrated. The model was further examined using sensitivity analysis for these flames to elucidate common reactions affecting its performance.

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Impact of the presence of potassium in cellulose under fast pyrolysis conditions

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Bioenergy can easily address the current energy challenge due to its great potential to contribute to the supply of the future energy demand in a sustainable way [1]. Biomass is majorly composed by cellulose, hemicellulose, lignin, extractives and a small amount of inorganic matter. Pyrolysis is a promising biomass upgrading technology since it can lead to the formation of solid, liquid and gaseous products, all usable for energetic purposes [2]. It is well known that the interactions between organic and inorganic components of biomass can affect the pyrolysis behavior by catalyzing or inhibiting several chemical reactions [3].

Many efforts have been directed to understand the pyrolysis process through numerical modeling [4]. There are a few studies that have focused on kinetic mechanisms of cellulose pyrolysis that are able to predict mass loss curves, product yields and product speciation [5]. However, the influence of interactions cannot be simple predicted on the basis of separate thermal behavior of the major biomass components [6]. Until very recently, these mechanisms gave little attention to the impact of inorganic interactions on the pyrolysis process. Leng et al. [7] studied the effect of KCl and $CaCl_2$ loading on the formation of reaction intermediates during cellulose fast pyrolysis in a wire mesh reactor. These authors proposed a modified kinetic mechanism for cellulose pyrolysis, based on the work of Ranzi et al. [5], which takes into account the primary catalysis of KCl and $CaCl_2$.

This study focus on the impact of the inorganic K element interactions on the fast pyrolysis of cellulose examining the relevance of these interactions in the numerical predictions. The experimental data of Leng et al. [7] is used as reference data. The authors doped cellulose with KCl and subjected the pure and doped cellulose samples to a fast pyrolysis process that was carried out up to a temperature of 873 K, at a heating rate of 100 K/s, where nitrogen was used as a career gas, in a wire mesh reactor. Numerical predictions were obtained by using the Bio-Polimi mechanism [5] and the Cantera reaction kinetics library [8]. Figure 1 shows the comparison between the mass loss curves of pure and doped cellulose samples and the predictions obtained with the Bio-PoliMi mechanism. The pyrolysis of the doped sample started at lower temperatures and increased the formation of char. A similar trend was observed previously by Gargiulo et al. [6]. Predictions of cellulose pyrolysis are in agreement with the experimental results of pure cellulose sample. It is clear that the K element affects the cellulose pyrolysis process, having a catalytic effect at low temperatures, but inhibits the volatile yield. The cellulose sub-mechanism of the Bio-PoliMi mechanism is modified based on the mechanism proposed by Leng et al. [7]. The comparison between the experimental and the latter numerical results provides further insights on the importance of the interactions between organic and inorganic biomass components in the kinetic mechanisms.

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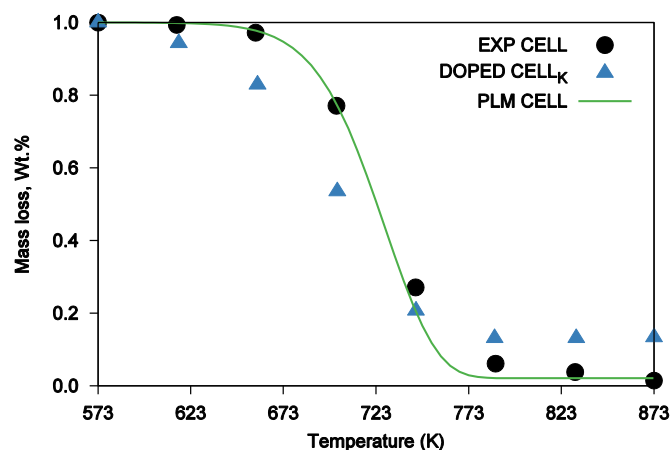
Figure 1. Comparison between the mass loss curves of pure and doped (with K) cellulose samples and the predictions obtained with the Bio-PoliMi mechanism.

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Kinetic investigation of the homogenous partial oxidation of CH_4/C_2H_5OH and $CH_4/n\text{-}C_7H_{16}$ mixtures

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Introduction

To reduce CO_2 emissions, major efforts are undertaken to increase the use of renewable energy. However, the associated fluctuating electricity generation, particularly by wind and solar power plants, leads to a discrepancy between electricity supply and demand. Therefore, processes that are able to store energy and allow flexible and adaptable power conversion need to be developed. One concept is to store energy in chemicals, e.g. by coproduction of useful chemicals in piston engines in addition to work and heat. Conversion reactions take place at uncommon reaction conditions. These include fuel-rich mixtures, high pressures and high temperatures. To investigate the fundamental kinetics of conversion reactions, fuel-rich mixtures of CH_4 are oxidized at different temperatures in a plug-flow reactor (PFR). Furthermore, the effect of C_2H_5O and $n\text{-}C_7H_{16}$ as additives is investigated. For the analysis of the gas-phase species after the chemical conversion, gas samples at the reactor outlet can be analyzed with a gas chromatograph. In order to prevent condensation of the samples they are heated to 100 °C until the injection starts.

Methods

The PFR consists of an inner quartz tube which is, as a precaution, surrounded by an outer pressurized stainless-steel tube. The reactor is heated by heating tapes, wrapped around two copper shells that in turn enclose the stainless-steel tube in order to realize isothermal conditions within the reaction zone. The experiments were carried out at 6 bar, 473-973 K and equivalence ratios of 2 and 20. In order to validate different reaction mechanisms for the atypical reactions conditions the experimental results are compared with simulations. For these simulations the zero-dimensional reactor module of Cantera [1] is used in combination with the reaction mechanisms of Li et al. [2] and Ranzi et al. [3].

Results and Discussion

The results of this work and previous studies [4] show that in the case of neat methane high temperatures (> 700 K) are necessary for methane consumption. Above these temperatures it is possible to produce synthesis gas (CO, H_2) and small amounts of oxygenated species like CH_3OH and higher hydrocarbons like C_2H_6 and C_2H_4 at both equivalence ratios. But, at $\Phi = 20$ higher amounts of C_2 species as well as traces of C_3 species were detected. CH_3OH is an useful raw material in the chemical industry and serves as a precursor for many other chemical compounds. Unsaturated hydrocarbons, however, could be used in terms of energy storage, because their enthalpies of formation are higher compared to the enthalpies of formation of the reactants. In addition, the detected C_2 and C_3 compounds indicate that C-C-coupling reactions occurred.

In order to investigate the effect of C_2H_5O and $n\text{-}C_7H_{16}$ on the partial oxidation process, 5 % of the methane fuel was substituted by the respective additive. Here it can be noted that the reaction temperature of methane was shifted by 150-250 K ($n\text{-}C_7H_{16}$) and 50 K (C_2H_5O)

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towards lower temperatures, that the highest methane conversion can be achieved with addition of n-C_7H_{16}, and finally that the composition of product gases changes. At $\Phi = 2$ higher yields of CO and H_2 with the addition of both, C_2H_5O and n-C_7H_{16}, are obtained. The CO production starts at lower temperatures in agreement with the lower start temperatures No significant change in the maximum yields of CH_3OH can be observed, but the production of CH_3OH occurs in a wider temperature range with n-C_7H_{16} addition. Finally, reasonable agreement between simulations and experiments can be found in CH_4, CO and CH_3OH trends, whereas the methanol yield is strongly overpredicted by the model.

At $\Phi = 20$, higher CO yields can be observed, if C_2H_5O is used as additive compared to neat methane oxidation. But higher yields of H_2, are observed with the addition of C_2H_5O. Besides, a CO and H_2 production is present at lower temperature, which again can be explained by the earlier reaction start. As mentioned before there are more C_2 species at $\Phi = 20$, compared to $\Phi = 2$. Using the example of C_2H_6, slightly higher yields can be achieved with the addition of C_2H_5O. Finally, the comparison between simulated and experimental data shows reasonable agreement in general trends, whereas the production of CO and C_2H_6 starts at much lower temperatures in the simulations, if n-C_7H_{16} is used as additive. Reaction pathways and the reactions responsible for the changes in the product composition are analyzed in detail from the reaction mechanisms.

Conclusions

The homogenous partial oxidation of methane and the influence of ethanol and n-heptane on the oxidation process was investigated. All experiments were performed in a flow reactor at 6 bar and 473-973 K at $\Phi = 2$ and $\Phi = 20$. Furthermore simulations were conducted in order to validate different reaction mechanisms and a chemical understanding is developed by analysis of the simulation results. It can be noticed that both additives significantly lower the reaction temperature and increase the yields of some interesting species. In general, the product gas consists of synthesis gas and small amounts of oxygenated species as well as higher hydrocarbons, whereas the latter are available in higher amounts at $\Phi = 20$. Finally reasonable agreement between simulated and experimental data could be found, even though the reaction mechanism had not been tested at these uncommon reaction conditions before. While overall product yields of the partial oxidation process are low, cogeneration schemes of energy and chemicals seem feasible from a chemical kinetic point of view.

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A modeling and experimental study of laminar premixed C4-flames - iso-butanol blended with 1,3-butadiene

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Abstract

As a response to increasing concerns about global warming resulting from the combustion of fossil fuels, renewable energy resources including alcohols are of major importance. Butanol isomers (1-, 2-, and iso-butanol) are of interest as a fuel additive to gasoline, due to their high octane numbers. In this context, the combustion characteristics of butanol has recently gained much interest for two reasons: (i) butanol are producible sustainable [1]; (ii) their use promise less sooting than hydrocarbons [2]. Studying formation and destruction pathways of soot is within the focus of current investigations. The addition of small hydrocarbons (1,3-butadiene) to single-ring aromatics (benzene) are considered as major steps in PAH-formation and growth reactions [3-4]. For these reasons, a comprehensive understanding of the combustion chemistry in flames fueled by blends of hydrocarbon/butanol is needed.

In the present work, the oxidation of 1,3 butadiene/iso-butanol flames was studied in a combined modelling and experimental work. The aim of the present study is to provide a detailed chemical kinetic reaction mechanism capable to describe the major pathways for butadiene and butanol oxidation as well as the formation of soot precursors and aromatics.

Detailed data on the chemical composition of three premixed, low-pressure (20-30 torr) flames, with different shares of iso-butanol ranging between 25% to 75% compared to butadiene in 50% argon, was used for validation of an in-house reaction model. Mole fraction profiles of reactants, major products, and intermediates including C3Hx and C4Hx radicals and mono aromatics were measured quantitatively as a function of height above burner surface employing flame-sampled molecular-beam mass spectrometry (MB-MS) utilizing photoionization with tunable vacuum-ultraviolet synchrotron radiation. The in-house chemical kinetic model is based on the reaction set used previously [5-9] and was enlarged by an iso-butanol sub-model to describe the oxidation three combined iso-butanol/1,3-butadiene flames [10].

Detailed kinetic modeling results are compared against flame-sampled molecular-beam mass spectrometry data obtained in three fuel-rich laminar premixed flames. The experimental data are obtained by utilizing photoionization by tunable vacuum-ultraviolet

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synchrotron radiation allowing the identification and separation of combustion species by their characteristic ionization energies.

The predictive capability of the reaction model will be discussed. The calculated mole fraction profiles for important species in the mass range from m/z=1 (H_2) to m/z=78 (C_6H_6) agree, in general, well with the experimentally observed profiles, under the current low-pressure, high-temperature conditions. Thus, the reaction model allows an assessment of the importance of various fuel consumption and formation pathways of aromatic species and their precursors by using reaction flux and sensitivity analyses.

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Revisiting 1-hexene low-temperature oxidation

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Since alkenes are important components of gasoline, literature shows that the low-temperature oxidation kinetics of C_5-C_7 linear alkenes has been frequently investigated. However the experimental studies concerning the low-temperature reactivity of the most studied C_5-C_7 alkenes, hexene isomers, which were obtained in a rapid compression machine [1] and in a jet-stirred reactor [2], are limited to stoichiometric conditions. While theoretical calculations have recently been made for several reactions important for alkene low-temperature oxidation (e.g. reactions of alkenes with OH radicals [3]), the last detailed kinetic models of hexene oxidation were published before 2011 by Mehl et al. [4] and by Bounaceur et al. [5][5].

The low-temperature oxidation of 1-hexene has been studied in a jet-stirred reactor for temperatures from 500 to 1100K, at atmospheric pressure, for equivalence ratios from 0.5 to 2 with a high dilution in helium. Product formation has been investigated using gas chromatography, but also by laser-single-photon-ionization time-of-flight mass spectrometry and *cw*-cavity-ring down spectroscopy. These two last techniques have allowed the quantification of ketene, C_1-C_3 alkylhydroperoxides, hexenyl hydroperoxides, C_6 unsaturated ketohydroperoxides, and hydrogen peroxide.

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Based on a previous automatically generated one [5], a new model has been developed for 1-hexene oxidation by updating some determinant reaction kinetics based on newly published theoretical calculations. This new model allows a good prediction of both most of the newly obtained results, as well as satisfactory simulation of literature data obtained for high-temperature oxidation in high-pressure jet-stirred reactor, rapid compression machine, and shock tube.

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Trying to understand the mechanism of combustion in innovative biofuels: Modelling the case of oxydized tetrahydrofuranes

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Based on the results of previous experimental works by using a rapid compression machine (RCM) and a jet-stirred reactor (JSR),[1] the chemistry associated to the low-temperature oxidation and ignition of tetrahydrofuran has been investigated. The reactions of 2-peroxy-tetrahydrofuran (2-OOTHF) and 3-peroxy-tetrahydrofuran (3-OOTHF) has been theoretically studied at CBS-QB3 level.[2,3] The formation of 2-oxo-tetrahydrofuran and 3-oxo-tetrahydrofuran are favorable pathways. However, considerable barriers of ~40 kcal mol^{-1} have to be overcome to produce such products. On the other hand, other products can also be obtained in which the rate determining step has lower barriers (25-30 kcal mol^{-1}). This is the case for the formation of 2,6-dioxabicyclo[3.1.0]hexane and succinaldehyde, which also give quite exothermic pathways.

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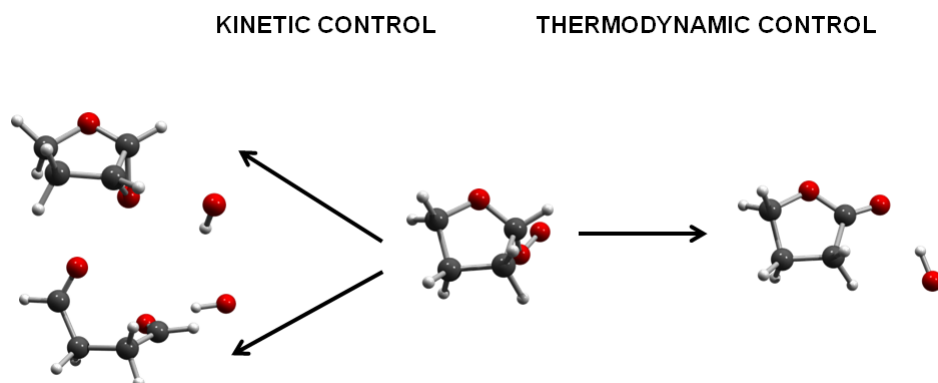
Most important products from 2-OOTHF.

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Experimental and modeling study of the soot formation process in very low sooting low pressure methane flames

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General aspects

We present recent results on the so called nucleation flames. These premixed flames produce incipient soot nanoparticles, identified by laser induced incandescence, that do not undergo measureable size increase from surface growth and coagulation. In these flames the soot mass increases along height above the burner only by nucleation from the gas phase. These flames are very useful to better understand the nucleation process.

Experimental setup

We used several experimental techniques to gain insights on the soot formation and growth processes, including the soot volume fraction that is measured in-situ by laser induced incandescence, and the chemical composition of the gas phase that is investigated ex-situ by jet-cooled laser induced fluorescence and using off-line secondary ion mass spectrometry in parallel. Particular attention is devoted to soot molecular precursors like polycyclic aromatic hydrocarbons.

Main results

The experimental results are compared to and analyzed with the help of kinetic modeling on two different flames, a *nucleation* and a *sooting* flame. Significant differences in the soot volume fraction and in the concentration profiles of hydrocarbons are observed in the nucleation flame with respect to the reference sooting flame that are related to the surface growth process of soot particles. In particular, we find that in the nucleation flame the soot particle diameter and the ensemble of identified hydrocarbons are constant all along the flame reaction coordinate, a behavior that can be well reproduced by modelling.

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Contribution of alternate Poly Aromatic Hydrocarbon (PAH) production routes in transportation fuels combustion

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Abstract

To better control Polycyclic Aromatic Hydrocarbons (PAH) emission and minimize their health and environmental effects, it is crucial to better understand their formation mechanisms. In the present work, we developed a new detailed chemical kinetic mechanism describing accurately both low and high temperature ignition and combustion of automotive and aviation fuels as well as the formation of PAH up to coronene, suspected to be major soot precursors. Surrogate mixtures containing n-decane, iso-octane and n-propylbenzene were selected to represent the above-mentioned fuels based on their capability to reproduce cetane numbers (CN) and threshold sooting index (TSI) of practical fuels. Including new reactions paths from recent studies [1,2] resulted in the improvement of mechanism predictivity over a wide range of experimental conditions (shock tubes, jet stirred reactor, burner stabilized premixed flames, and freely propagating premixed flames). The mechanism is able to simultaneously reproduce PAH mole fraction profiles, ignition delay times and laminar flame speeds for a variety of fuels ranging from methane to Diesel fuel.

Following the mechanism validation, reactions path analyses were performed to identify aromatics formation pathways for practical as well as laboratory fuels. The impact of the fuel structure and reaction progress (e.g. height above the burner, HAB) on the respective importance of aromatics formation reaction routes were also characterized, highlighting the contrasted contributions of phenyl + vinylacetylene and benzyl + propargyl steps. In line with recent experimental findings [3], a path involving dibenzofuran was found to play a key role in aromatic production in jet-A1 flame, indicating a significant involvement of such species in PAH production in middle distillate combustion.

Key Words: Transportation Fuels; Surrogate; Chemical kinetic mechanism; PAH
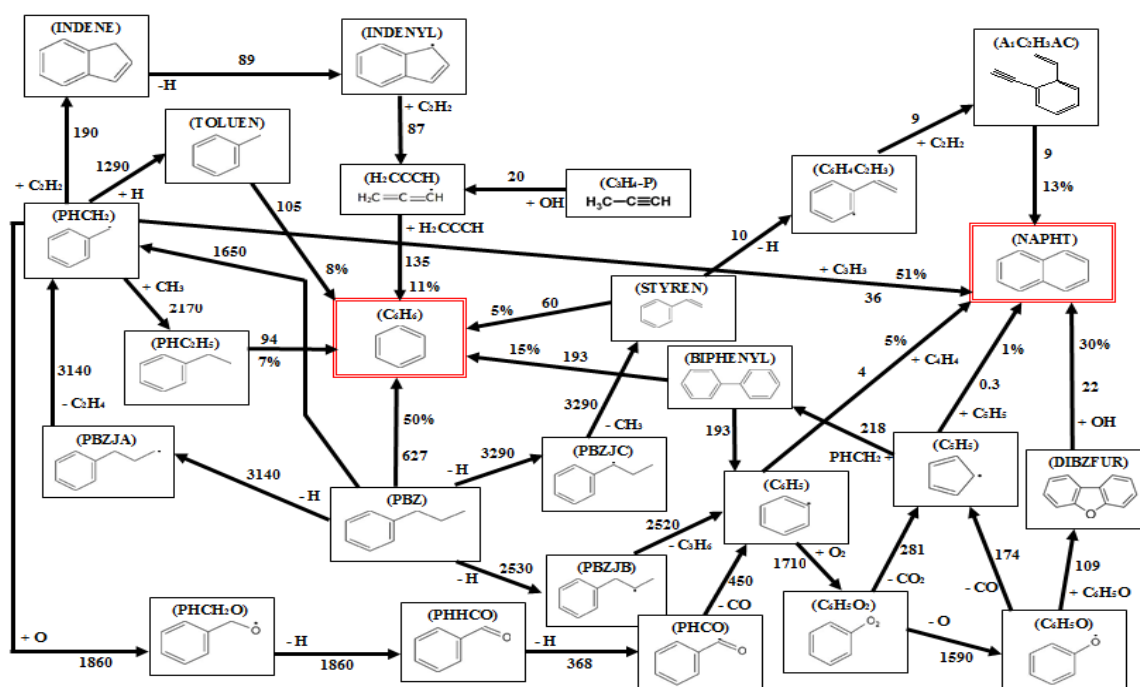
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Fig.1. Major benzene and naphthalene formation pathways in jet-A1 fuel flame: HAB=0.4 mm (56.2% of jet-A1 fuel conversion); φ=1.7; P= 1atm ; The absolute net reaction fluxes are expressed in nanomole per cubic centimeter per second and the relative contribution of reactions directly involved in benzene and naphthalene production are indicated in percent.
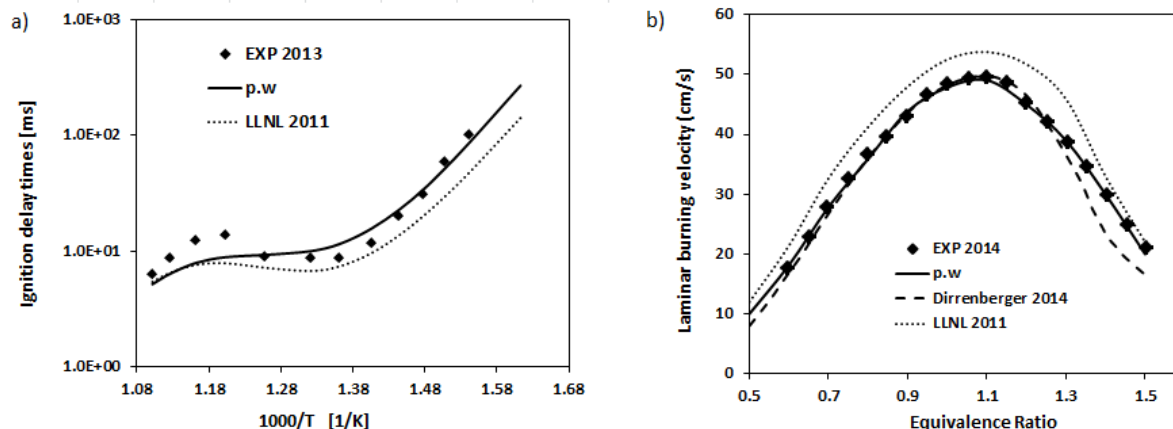

Fig.2. a): Ignition delay response of gasoline in a rapid compression machine: φ=1 ; P = 20 bar ; T = 640-900 K ; b): Laminar burning velocity of gasoline : P = 1 atm ; T_u = 358 K.

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Surface Composition and Reactive Oxygen Species (ROS) Generation: Evaluation of Health Risks of Soot Nanoparticles based on quantitative interfacial composition

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The conditions of hydrocarbon combustion determine to a large extent the bulk and interfacial properties of the resulting combustion aerosol (soot) including the surface composition. Our **goal is to understand the human health effects of emitted combustion aerosol nanoparticles (NP) in relation to the surface composition of the particle-air interface** which we understand as the gateway to chemical reactivity. In order to establish this relationship we need
(a) molecular information on the surface functional groups responsible for the chemical reactivity of soot, and
(b) the reaction rate of a diagnostic chemical reaction (proxy) in aqueous solution such as the oxidation of DTT (DiThioThreitol) that simulates the deleterious antioxidant oxidation (destruction) leading to Reactive Oxygen Species (ROS) in the presence of soot and air oxygen [1]. We are limiting our scope to NP's from a Diesel engine (powered by standard Diesel and Hydrotreated Vegetable Oil (HVO) fuels) and a few soot reference samples (GTS (Graphitic Thermal Soot)-6, GTS-80 and Printex XE-2B amorphous carbon) [2,3].

Regarding (a) we have used a titration technique using four reactive probe gases interacting with the solid samples in a Knudsen flow reactor [4]. We are focusing on NO_2, O_3, HCl and CF_3COOH as reactive probe gases: NO_2 reveals the surface composition of **strongly** reducing surface functional groups because NO_2 is a weak oxidizer whereas O_3 retrieves the **total number** of reducing groups owing to its strong oxidizing capacity. CF_3COOH is a stronger acid than HCl in the gas phase so that CF_3COOH neutralizes all bases, weak and strong, whereas HCl only neutralizes strong bases.

Regarding (b) the rate of DTT oxidation by dissolved O_2 in aqueous solution correlates unexpectedly well with the number of **strongly** reducing sites. This indicates that the autoxidation of antioxidants of reduced surface sites, for instance hydroquinones of large extended polycyclic aromatic hydrocarbons (PAH) is rate-limiting. When measuring both the consumption of DTT and dissolved O_2 we conclude that quinones and hydroquinones derived from polycyclic aromatic hydrocarbons are not consumed but are involved in efficient redox cycling given the excess O_2 at atmospheric conditions with turnover numbers of 30-600 per catalytic site depending on the type of soot NP's [1]. Therefore, the

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functional groups on NP's act as (redox-cycling) **catalysts** in the air oxidation of DTT and are in principle not consumed. However, owing to the limited turnover number per catalytic site we conclude that the catalyst is slowly consumed in competing side reactions that irreversibly destroy active sites.

This oxidation will lead to ROS and affect the lifetime, hence the abundance of antioxidants *in vivo*, and may lead to deleterious health effects. In addition, the rate law for O_2 consumption has been verified for two soot NP's and is given by $-d[O_2]/dt = k[O_2]^2 [DTT][NP]$ [1]. The quadratic dependence of the rate on O_2 points towards a sequential interfacial reaction involving semiquinone free radical. Hydroquinone oxidation is the rate-limiting step in the overall catalytic surface oxidation of DTT by dissolved oxygen (see above). We are now able to claim that both Diesel and HVO fuels and GTS-80 [5] represent an accrued risk for ROS production compared to the other characterized NP's of this study owing to the large abundance of strongly reducing surface functionalities. The simultaneous presence of weakly basic functional groups (pyrones or the combination of a carbonyl group with an aromatic ether oxygen) and quinones (two carbonyl groups), the presence of which have been independently verified using FTIR absorption spectroscopy in soot samples, leads to free radicals on the surface of soot NP's that are stable under environmental conditions (Environmentally Persistent Free Radicals (EPFR)). The combination of strongly reducing (oxidizable compounds such as hydroquinones derived from PAH's) with weakly basic properties (such as pyrones) will lead to a conjugated chemical system having an odd number of electrons under certain topological conditions. Two important factors are (1) "closed shell" structure of the quinone corresponding to its ground state by judiciously choosing the peripheral position of the carbonyl groups, thus excluding biradical structures, and (2) an odd number of aromatic ether oxygens located in whatever position of the periphery of the conjugated network. The minimum requirement for the existence of an EPFR satisfying the obtained interfacial composition is a PAH having two carbonyl and a single ether oxygen in conjugation. The conditions for the possible existence of stable free radicals leading to EPFR and the corresponding relative stability of the peroxy free radicals will be presented.
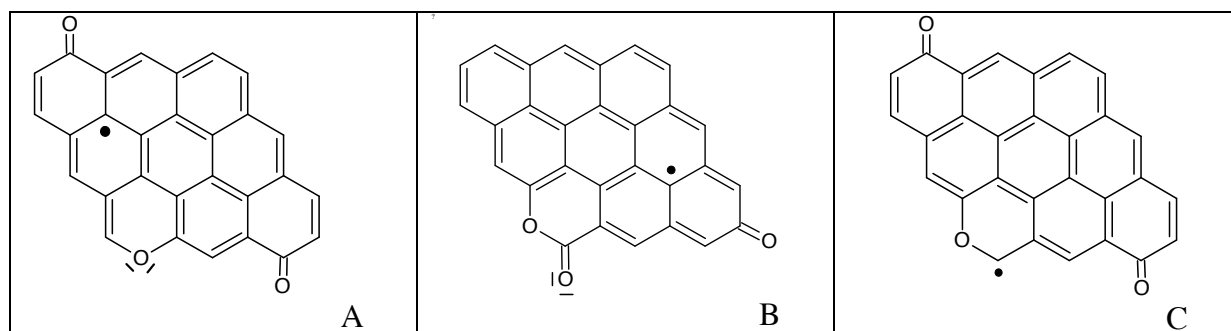

Table 1: Possible isomeric structures of a conjugated aromatic hydrocarbon having an odd number of π-electrons giving rise to Environmentally Persistent Free Radicals (EPFR) which may in part constitute ROS.

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Impact of methyl butanoate oxidation on NO formation in low pressure flames

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General aspects

This work is focused on the study of the environmental impact of methyl esters used as biodiesel and concerns more particularly the kinetic of nitrogen oxides formation during the methyl esters combustion in flame conditions. The study is focused on prompt-NO formation. Prompt-NO route is thoroughly connected to CH radical formation through the initiation reaction between CH and N_2. The aim of this study is to test detailed kinetic mechanisms for the prediction of NO formation during the oxidation of methyl butanoate (MB), a compound chosen as model for biodiesel. Structure analysis in laminar low pressure flames is performed by using laser diagnostic techniques (Laser Induced Fluorescence, LIF and Cavity Ring-Down Spectroscopy, CRDS) and analytical techniques (Gas Chromatography, GC). Experimental results are compared to simulated species profiles using Chemkin-II/Premix code and considering two detailed mechanisms [1,2].

Experimental setup

Three stoichiometric $MB/CH_4/O_2/N_2$ premixed flames were stabilized on a McKenna burner in low pressure conditions (53.3 mbar). The relative MB mole fraction with respect to the total fuel ($MB+CH_4$) was added between 0 and 50%. Total gas flow rate was fixed to 320 L/h and nitrogen dilution was kept to 65%. GC technique allowed to measure few stable species after gas probe sampling. Relative mole fraction profiles of NO and CH were measured by using in situ LIF technique. Absolute quantification was performed by NO addition in the cold mixture, and by using CRDS for CH radicals. Temperature profiles were determined by using NO-LIF thermometry.

Main results

Temperature in the burnt gases does not exceed 1800K insuring that thermal NO production is negligible in the investigated flames, as confirmed by the flat profile of NO mole fraction in the burnt gases. Addition of MB in the $CH_4/O_2/N_2$ flame yields a decrease of about 20% of NO in the burnt gases. Similarly we observed the same decrease of the CH peak mole fraction.

Two detailed mechanisms previously validated in various experimental conditions [1,2] have been completed with the NO formation sub mechanism NOMecha2.0 [3]. Both mechanisms predict a decrease of the NO mole fraction in the burnt gases as the initial amount of MB increases, in agreement with the trends experimentally observed. Modelling results show that both calculated NO and CH profiles issued from [1,3] are in much better agreement with the experimental ones than those issued from [2,3].

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Reaction pathway analysis shows that MB and CH_4 present the same ability to produce CH_3 radicals. CH radicals are presumably issued from the C1 sequence. In stoichiometric mixtures, MB addition yields a decrease of the total fuel which results in decreasing NO in the burnt gases.

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Impact of calcium and potassium on single particle ignition behaviour of biomass fuels

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Introduction

Biomass is a renewable and CO_2-neutral energy source already used for energy production. However, there are a number of issues such as preparation of biomass and/or ash-related matters during and after combustion that hinder the clean and efficient utilization of biomass in energy applications [1]. Biomass ashes usually include alkali and alkaline earth metals such as Ca and K; and despite these compounds being typically present in low concentrations, in comparison to main biomass components (carbon, hydrogen and oxygen), they may affect or modify the whole biomass ignition/combustion process and/or the formation and emission of pollutants [2]. In this context, this work aims to evaluate how the ignition behaviour of biomass is affected by the presence and concentration of alkali and alkaline earth metals (Ca and K).

Methodology

This work includes the analysis of raw grape pomace, demineralized biomass and biomass doped with 0.1% wt., 0.5% wt., 1.08% wt. (equal to Ca concentration in the raw biomass), 3% wt. and 6% wt. Ca and 0.1% wt., 0.5% wt., 0.82% wt. (equal to the K concentration in the raw biomass), 3% wt. and 6% wt. K. All samples were sieved into the 200-250 μm size range and dried before the tests. The tests were carried out in an optical flat flame Mckenna burner at $\lambda = 1.3$ and two conditions: T1 (1575 K gas temperature and 5.4% dry vol. O_2 at the ignition zone) and T2 (1775 K gas temperature and 5.2% dry vol. O_2 at the ignition zone). Figure 1 shows a schematic of the experimental setup used. The general description of the system can be found elsewhere [3]. A Matlab routine was used to calculate the ignition delay time following the luminosity criterion showed in Figure 2.
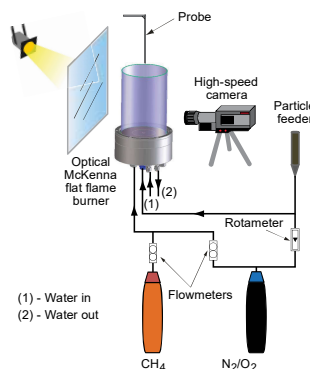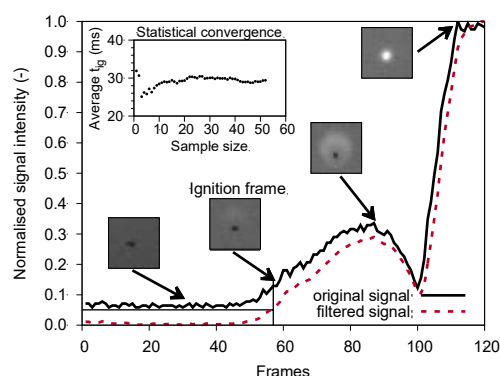

Figure 1. Schematic of the experimental setup.

Figure 2. Post-processing test criterion.

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Results

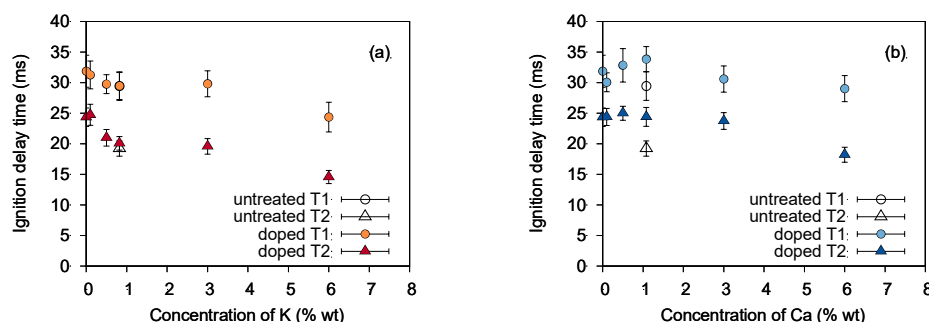Figure 3 shows the ignition delay time for all the samples and conditions of this work.

Figure 3 Ignition delay time for operating conditions T1 and T2 for raw grape pomace (untreated), demineralized biomass (0% wt. minerals) and for the biomass doped with the different concentrations of K [a] and Ca [b]. Vertical bars represent 98% confidence statistical error.

The results indicate that the influence of K (Figure 3a) and Ca (Figure 3b) on the single particle ignition delay time of biomass depend not only on the given earth metal considered but also on its concentration. In general, the ignition delay time of biomass decreases with increasing K content, and for 6% wt. K, the ignition delay time is even lower than that for the raw biomass. In the case of Ca, only for the highest Ca content (6% wt. Ca) the ignition delay time of biomass is decreased, and shows an ignition delay time almost equal to that of the raw biomass. Similar tendencies are obtained for the two conditions analyzed in this work, but with relative higher ignition delay times for the lowest temperature (T1). The results also evidence the promotion of the ignition of raw biomass as compared with the demineralized biomass, and thus the significant role of minerals on biomass combustion.

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On the kinetics of thermal NO formation

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Introduction

Nitrogen oxides constitute an important category of anthropogenic pollutants [1]. NO is mainly formed in combustion systems, including power station furnaces and internal combustion engines. In hydrocarbon combustion systems, NO can be formed in four chemically different routes from the N_2 of air. At high temperature, NO is formed mainly in the thermal (Zeldovich) route.

Motivation

Although the thermal route was first recommended 70 years ago [2], its quantitative kinetics is still not known. Recently, Abian *et al.* suggested a rate expression of reaction $N + NO = N_2 + O$ based on their flow reactor experiments [3]. The NO concentration was measured in a $N_2/O_2/H_2O$ mixture in the temperature range of 1700 K – 1810 K at atmospheric pressure. The rate coefficient was assumed to be temperature independent in this range, fitted for each experimental point based on the nitrogen chemistry model of Klippenstein *et al.* [4], and averaged. Our aim was to re-evaluate these experimental data, by taking into account also other available experimental results simultaneously.

Optimization method

Turányi *et al.* developed [5] a new optimization approach for the determination of rate parameters. It can provide reliable rate parameters based on experimental and theoretical data, and the temperature dependent uncertainty for the determined rate coefficients. The main features of this approach are:

(i) direct experimental data and results of theoretical calculations are used for the determination of the joint prior uncertainty domain of the Arrhenius parameters;
(ii) if possible, all published related indirect experimental data are used;
(iii) direct experimental data points and theoretical results are also considered at the optimization;
(iv) all Arrhenius parameters A, n, E of the important reactions are fitted;
(v) the joint uncertainty of the fitted parameters is calculated, resulting in the domain of posterior uncertainty.

Data used

The thermal NO formation route was also investigated experimentally by Bowman [6] and Engleman *el al.* [7]. We found that these data are not appropriate for the quantification of the thermal NO formation rate coefficients. Therefore, we used only the data of Abian *et al.* as indirect experimental data. Based on local sensitivity analysis at the conditions of the Abian *et al.* experiments, the rate parameters of elementary reactions $NO + N = N_2 + O$ and $N_2O + O = 2\ NO$ were selected for the optimization. Direct experiments and theoretical results for these reactions from Davidson and Hanson [8], Michael and Lim [9] and Gonzalez *et al.* [10] were also utilized in the optimization.

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Results

The optimization led to a better description of the experimental results of Abian *et al.*. An example for the comparison of the measured and simulated NO concentrations is provided in Figure 1.

Figure 2 shows that in the temperature range of the experimental data, the rate expression of reaction NO + N = N_2 + O can be determined with high accuracy.
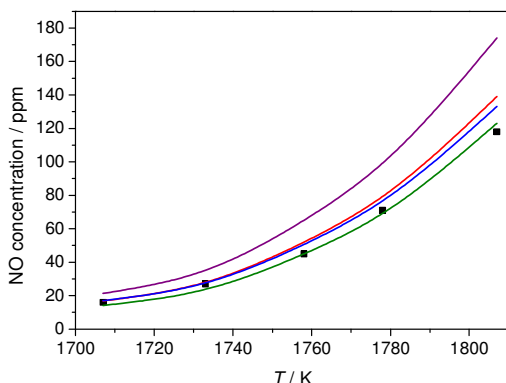
Figure 1 Comparison of the measured NO concentration (black squares, Abian *et al.* [3]) and the simulated values (purple line: Konnov-2009 mechanism [11], red line: Abian *et al.* mechanism [3], blue line: GRI 3.0 mechanism [12], green line: optimized mechanism. Initial mixture composition: 0.45 % O_2, 99.05 % N_2, 0.5 % H_2O.
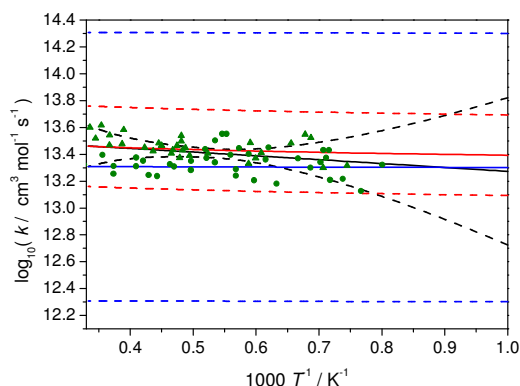
Figure 2 Arrhenius plot of reaction NO + N = N_2 + O. Black lines: optimized values (this work), red lines: rate expression recommended by Abian *et al.* [3], blue lines: the prior rate expression. Dashed lines: the respective 3σ uncertainties. Experimental data: green triangles, Davidson and Hanson [8]; green circles, Michael and Lim [9].

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Emissions of polycyclic aromatic hydrocarbons (PAH) during biomass combustion in a drop tube furnace

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INTRODUCTION

Biomass is one of the most abundant and used sources of renewable energy in the world with reduced impact on global warming. It is becoming more relevant as an energy carrier due to its high diversity and availability. Most processes using biomass are optimized to woody biomass; however, due to economic and environmental reasons, only a part of the available forest biomass can be used. In this context, the use of agricultural residues for energy purposes is an interesting issue. The extreme variability of the biomass feedstock demands for an extensive investigation on the impact of its composition in their combustion behavior. Biomass and especially wood are considered to be a major emission source of local pollution, namely, particulate matter (PM) and polycyclic aromatic hydrocarbons (PAH), which are considered as a big concern and are associated to highly carcinogenic and mutagenic compounds [1].

EXPERIMENTAL

The combustion experiments were carried in a drop tube furnace (DTF) using the following biomass fuels: rice husk, wheat straw, *Platanus* residues, kiwi residues, furniture residues, olive residues, sugar cane residues and grape pomace. The DTF used here is described in detail elsewhere [2]. Briefly, the DTF is an electrically heated ceramic tube with a water-cooled injector, placed at the top end of the DTF, with the purpose of feeding the biomass and the oxidizer (air) to the combustion chamber. In this study, measurements were carried out for the mentioned biomass fuels for DTF wall temperatures of 900 °C, 1000 °C and 1100 °C. The solid fuel feeding rate was set to 23 g/h, the total air flow rate was set to 4 L/min, ensuring a residence time in the DTF of around 2 seconds. The PAH collection started after the DTF reached steady-state conditions, with each measurement lasting for about 15 minutes.

The soot-PAH collection system consisted of a quartz microfiber filter (≤ 1 μm) connected to the outlet gas stream of the DTF, where the particulate matter were collected, followed by an XAD-2 resin packaged placed in a thin quartz tube. Later, the samples were extracted, concentrated and analyzed in a GC-MS system, considering the sixteen PAH classified by the Environmental Protection Agency (EPA) as priority pollutants and following the procedures described by Sánchez et al. [3]. Briefly, the procedure for extracting the PAHs from the samples is based on the Shoxlet extraction, which lasts 24 hours, using a total amount of 250 mL of DCM (dicloromethane), followed by concentration and separation, identification and quantification of the PAHs in the GC-MS system.

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RESULTS & CONCLUSIONS

Figure 1 shows the total PAHs collected (resin XAD-2 + filter particles) from the combustion of the different biomass fuels in the DTF at the three different temperatures of the reactor. The results are fairly similar for all biomass fuels at the same temperature, except for the furniture residues, which might had paints or varnish that may had contributed to the high PAH emissions. Figure 2 shows a comparison between the total PAHs for the different biomass fuels and its toxicity equivalent (TEQ), which is defined as the sum, extended to the 16 EPA-PAH, of the products between concentrations and TEFs (each single PAH has a reference value for toxicity). TEQ expresses the carcinogenic effect associated with the exposure to PAHs. A direct relation between the total amount of PAH and the TEQ value is found.
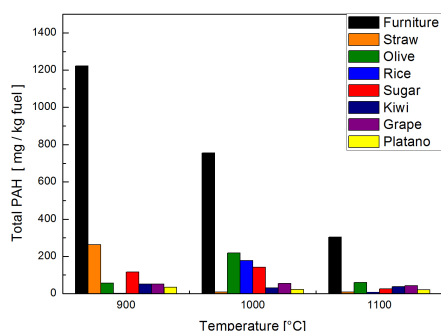

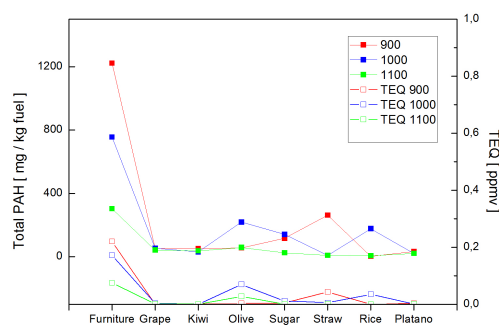*Figure 1: Total PAHs for all biomass fuels at three DTF wall temperatures.*

Figure 2: Comparison between total PAHs and its toxicity equivalent (TEQ).

ACKNOWLEDGEMENTS

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Preparation of C_2H_2 soot samples for cytotoxicity analysis.

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INTRODUCTION

Soot class includes particles of different sizes that can contain polycyclic aromatic hydrocarbons (PAHs), compounds known for being extremely harmful for human health [1]. Therefore, it is important to characterize soot emissions in order to acquire knowledge of its nature and progress on its minimization strategies.

Acetylene is one of the recognized main precursors of soot, and thus, it is easily found in early steps of most of the soot formation processes. For this reason, we have chosen acetylene soot as representative of the soot formed under many combustion conditions. The soot samples chosen are produced in the pyrolysis of 5% C_2H_2 at 1000 ºC [2] and have been characterized through a number of techniques typically used in the characterization of solids, i.e. SEM, TEM and HRTEM. Characterization of the C_2H_2 soot samples [2] used in the present work indicates that the soot samples used has high C/H ratios and graphitic structure.

Additionally, in order to further evaluate the impact of soot on human health, toxicological analyses can be carried out by investigating the behavior of human cells when these are in contact with carbonaceous nanoparticles. With the objective of performing a study of cytotoxicity consisting of a cell culture exposed to pollutants, and evaluate the end of the cell division process and the activation of the cell death process occurring through necrosis (the cell membrane is broken and the cell dies rapidly) or apoptosis (the cell activates a programmed death), a proper preparation of the samples is needed, which is the aim of the present work.

EXPERIMENTAL METHOD and RESULTS

Soot was first analyzed by FTIR and UV-vis analysis. The IR spectrum in Fig. 1a shows a characteristic broad peak in the range of wavenumber 1100-1600 cm^{-1} ascribable to C=C bond. So, the absence of H and O content indicates that this soot is extremely graphitic and hydrophobic. UV-vis confirmed the strong graphitic character of the soot under analysis.

Soot powder was then dispersed in bidistilled water in order to prepare samples for toxicologic studies. No other solvents were used to avoid interactions of the solvent with cells but to enhance the stability of the suspension and avoid the formation of aggregates and deposits a surfactant was necessary.

The surfactants used were sodium dodecyl sulfate (SDS) and dimethyl sulfoxide (DMSO). Two samples were prepared for each surfactant: the objective sample with soot and one control sample without soot. Different soot and surfactant concentrations were tested in order to optimize the ratio, which resulted to be of 20 µg/ml of SDS plus 20 µg/ml of soot in water and 10% vol. of DMSO in water plus 20 µg/ml of soot.

The preparation of the two samples consisted of the following steps: 1) Soot addition to the water+surfactant solution, 2) Sample sonication for 3 days, 3) Filtration of the samples with a

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paper filter (2.5 µm), 4) Sample sonication for 1 day, 5) Filtration of the samples with a paper filter (2.5 µm) and 6) Sample sonication for 3 hours.

After this, absorbance measurements were carried out to evaluate the dispersion of soot in the liquid samples, using a spectrophotometer. The spectra in Figure 1b show that the relative concentrations chosen for soot and surfactants allow having the same degree of soot dispersion in both samples. In fact, both profiles have the characteristic peak at 280 nm and a broad band at 315 nm. A comparison between soot+surfactant/water and surfactant/water samples shows that the peak and broad band are due to the carbonaceous material present in the samples and not to the surfactants.
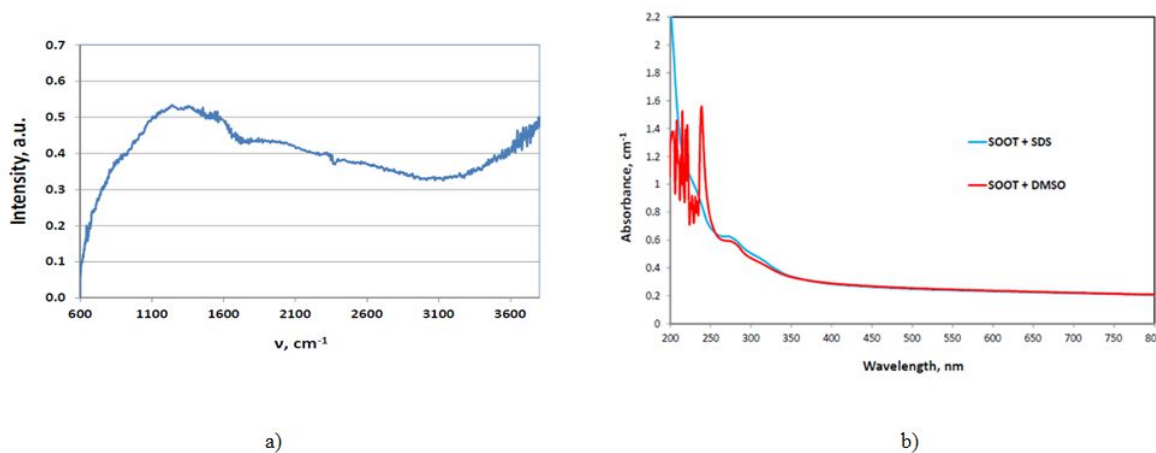

Figure 1: a) FT-IR spectrum of soot powder from acetylene pyrolysis. b) Absorbance spectra for Soot-SDS-water (blue line) and Soot-DMSO-water (red line) samples

Additional tests (Dynamic Light Scattering) were perfomed to determine the size distribution of the particles effectively suspended in water+surfactant solutions. The sizes of the suspended particles ranged from 20nm up to about 300nm with a mean size of the particle agglomerates ranging from 80 to 120nm, in excellent agreement with soot powder characterization [2]. Murine macrophage cell line was selected in order to evaluate in-vitro secretion of cytokines when the cells are in contact with the above mentioned soot samples. Preliminary tests performed at the Dipartimento di Farmacia of Università degli Studi di Salerno showed that DMSO does not interfere with cells making the water+ DMSO solution a valid method to suspend soot particles for toxicological studies.

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Laser-based and molecular beam sampling diagnostics for studies of combustion synthesis: from nanomaterials fabrication to syngas production

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Combustion is an important synthetic tool providing a convenient route for generation of a plethora of lucrative products ranging from nano-sculpted materials with tailored functionalities to syngas for liquid fuel production. With the start of the nano-age, interest in gas-phase-synthesized particles increased and more focus has grown on size effects of nanostructured catalytic materials. Flame synthesis been shown to be a useful route for the production of single-walled nanotubes, quantum dots and a wide variety of nanostructured ceramic oxides for catalysis and electrochemical applications. In addition, fuel-rich combustion (exothermic process of partial methane oxidation) is in the base of a novel technology for conversion of biogas and natural gas to syngas (mixture of hydrogen and carbon oxide). The syngas production is a first step toward the set-up of Gas-to-Liquid (GTL) process, which includes also the Fischer-Tropsch or similar process where syngas is converted to liquid hydrocarbons. Detailed understanding of the mechanisms governing these processes, based on the input gained from detailed measurements, based on state-of-the-art diagnostics is a necessary pre-requisite for intelligent combustion design. Here we highlight our recent work, where several techniques, based on molecular beam sampling, laser diagnostics and their combination are employed. These measurements yield experimental data directly comparable with the predictions of detailed kinetic simulations, enabling validation and improving our understanding of the underlying kinetic mechanisms. Specifically, we show by consolidated use of Intracavity Laser Absorption Spectroscopy and Quartz crystal microbalance diagnonstics combined with particle mass spectrometry analysis that in contrast to the commonly accepted paradigm, postulating the decomposition of the precursor followed by oxidation of the nascent Fe-atoms and late formation of iron oxide nanoparticles, the actual synthesis mechanism is considerably more involved and includes early formation of iron clusters [1,2]. We demonstrate how varying the synthesis conditions (e.g. fuel/stoichiometry/flow rate) allows to manipulate the particle formation mechanism. We present new detailed experimental data of absolute $^1CH_2$ and HCO radicals concentrations in wide range of very rich methane/air flame operating conditions that allow thorough analysis and of existing mechanisms of methane oxidation and their validation under fuel rich combustion regime[4,5]. Finally, we demonstrate optical diagnostics system for real time monitoring of CO/CO_2 ratio based on Fiber Laser Intra-Cavity Absorption Spectroscopy. Fast and reliable real time determination of CO/CO_2 ratio is crucial for evaluation of the performance of syngas production based on partial methane oxidation technology, since it serves as a measure

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completeness of combustion. By conducting experiments in a temperature-controlled flow-cell we have convincingly demonstrated that FLICAS based on an Erbium doped broadband laser, capable of being tuned in the range of 6350-6450 cm^{-1}, can be used for simultaneous CO and CO_2 absolute concentration and thermometry measurements[6,7].

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Exploring the performances of graphene-like layers as chemiresistive sensing material for volatile organic compounds (VOCs) detection.

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Volatile organic compounds (VOCs) represent a broad category of chemical compounds released into the atmosphere by a number of sources (industrial processes and incomplete engine combustion), some occurring naturally (evaporation form landfill sites). The detection and quantification of VOCs thus is crucial for the air quality monitoring.

Amongst the nanostructured gas sensing systems, carbonaceous nanomaterials have proved to be promising in the production of high performance chemical sensing due to their electrical and structural properties (high surface area, high chemical and thermal stability and functionalization capability). In the recent years graphene and related materials (GRMs) have been employed in many sensing experiments and they have been exploited for the detection of a widespread range of chemicals, including VOCs [1]. In this framework, reduced graphene oxide (rGO) played as main actor, because of the specific interactions with gas molecules driven by the presence of chemical functionalities in its structure [2].

In this work, we present the characterization as sensing layer of a material named Graphene-like (GL) layers that combines the graphene structure (a defect-free basal plane) with the presence of oxygen functional groups, mainly carboxylic, on the layer edges. GL layers consist in water-stable small graphenic fragments (composed by 3 or 4 stacked graphene layers) able to self-assemble in thin film on surfaces after drying [3,4]. In this work, GL layers were obtained as stable aqueous suspension through two-step strategies starting from a nanostructured carbon black (CB): oxidation/chemical reduction (involving hydrazine as reductant) and oxidation/solvothermal reduction (involving 1-methyl-2-pyrrolidinone, NMP) approaches. In both cases, the oxidation step destroys the CB backbone producing small graphenic fragments and the following reduction step partially restores the graphenic network, improving the electric conductive proprieties of the layers. GL layers were investigated as chemiresistive sensing material for the detection of selected VOCs, namely ethanol and acetone, in ppm levels. Ethanol and acetone have been chosen because they are included in the list of the VOCs that are of concern as both indoor and outdoor air pollutants. Among the different VOCs, ethanol is considered one of the most abundant. Ethanol was traditionally originated from distilleries and foundry plants but its recent incorporation in gasoline has increased the emissions of unburned ethanol to the atmosphere. Ethanol usually is not considered an extremely harmful pollutant, but at concentrations above 1000 ppm can cause severe health problems and not negligible environmental effects.

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The sensing experiments were performed under atmospheric pressure, in a dry air and at room temperature and demonstrated that the sensing capabilities are related to morphological and chemical features of the surface. The investigated materials showed different sensitivities to vapors exposure, as reported in Figure 1.
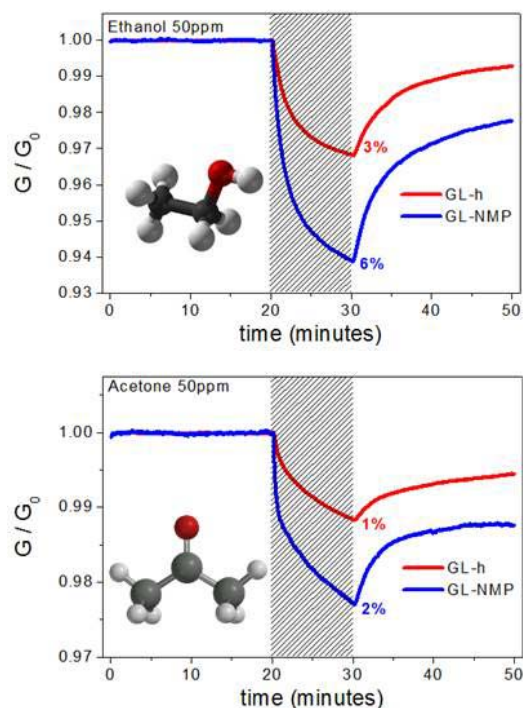

Figure 1: *Sensing performance at room temperature of GL-h (GL produced by chemical reduction with hydrazine, red line) and GL-NMP (GL produced by solvothermal reduction with NMP, blue line) film based devices at 50 ppm of concentration in dry air for a) ethanol and b) acetone.*

The results showed that GL layers are a promising candidate for the detection of low concentration of VOCs at room temperature. Characterizations with Atomic Force Microscopy and X-ray Photoemission Spectroscopy suggest a combined role of surface functional groups and morphology in determining the remarkable recorded properties.
The present experimental investigation paves the way to VOCs sensing optimization using economic and easily scalable materials and it is very promising taking into account the few available reports on the VOCs detection in ppm level at room temperature relying on chemiresistor devices based on similar sensing layers.

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Diagnostic of high-temperature flows using ultrasensitive cavity Ring-down spectroscopy

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The spectroscopic diagnostic and characterization of high-temperature gaseous environments such as hot atmospheres (Hot Jupiter exoplanets, circumstellar envelopes), hypersonic shock layers forming on the front of reentry bodies or combustion gases, are partly based on the use of high-temperature spectroscopic databases which are still incomplete for a large variety of relevant molecular species such as small hydrocarbons.

We have developed a High Enthalpy Source (HES) capable to heat gases up to 2000 K. The HES is coupled to an ultrasensitive cavity ring-down spectrometer (CRDS) operating between 1.5 and 1.7 microns [1, 2]. This new and original experimental set-up is used in two different and complementary ways:
- Coupling hypersonic flows to CRDS: A hypersonic flow is generated by expanding the heated gas into a vacuum chamber. As a result, the enthalpy of the gas is converted into kinetic energy leading to a high-velocity flow. Interestingly, this energy conversion is accompanied by a very strong decoupling of the internal degrees of freedom of the expanded gas. Its rotational temperature reaches few kelvins whereas its vibrational temperature remains almost unaffected by the cooling, i.e. close to the initial temperature of the gas (1000 - 1500 K). This very strong non-equilibrium situation is of particular interest to access the structure of the excited vibrational energy levels of the probed molecule by simplifying the rotational lines structure of the hot bands.
- Coupling hypersonic Post Shocks to CRDS: a stationary shock wave is formed by inserting an obstacle in the hypersonic flow. The gas is suddenly reheated and recompressed by crossing the shock wave. The rotational temperature reaches a value close to the vibrational one. The shock layer located between the shock front and the obstacle is probed by CRDS.

A series of preliminary results [1, 2], with a particular emphasis on methane, will be presented to illustrate the potential of this new experimental approach.

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Experimental investigation of OH* chemiluminescence intensities in premixed natural and producer gas flame

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Introduction

Processing of biomass by means of gasification allows to obtain producer gas with high hydrogen and carbon monoxide content. Further the producer gas could be used to substitute natural gas in various combustion devices. Utilization of novel fuel types, in particular – biomass-derived producer gas, requires understanding of the specifics of the combustion process in order to design novel burners for these fuel types or adapt the existing ones. One of most promising non-intrusive combustion process optimization technique is flame chemiluminescence monitoring. According to [1] ratios between various signals (for example, the ratio OH*/CH*) corresponding to light collected at different wavelength are commonly proposed as a reliable parameter to monitor a wide range of practical flames. OH*, CH* and C_2* radical chemiluminescence intensities show monotonously increasing trends with the air–fuel equivalence ratio [2]. In addition, if spectra are collected from more than one direction at same time it is possible to do a computed tomography of chemiluminescence and use it to obtain the 3D, instantaneous, visible chemiluminescence profile of a flame [3]. The aim of this work is to apply 3D flame chemiluminescence scanning technique to compare OH*, CH* and chemiluminescence intensity values along flame when using natural gas and producer gas mixture. This work presents comparison of chemiluminescence along flame from five different angles registered at same time with optical fiber ant spectrograph system.

Methodology

The experimental investigations were performed using the experimental setup consisting of an air/gas supply system, a lab scale gasification reactor system for producer gas supply, a combustion chamber, and a flame optical analysis system. The entire combustion process was observed by an optical system, which produced the output data for analysis of OH* spatial distribution in flame. For capturing images, the ICCD (Intensified Charge Coupled Device) camera was used. The sensor was digitally divided in to 5 equal areas to collect light from each of 5 optical fibers. Single frame exposure was set to 5 s, and 10 frames were accumulated into a single image for each flame condition at 20 measurement planes along flame height. Multiple frames were recorded for each combustion and imaging regime (fuel mixture composition, fuel and air flow rates, selected measurement plane) in order to minimize the effect of possible flame instability. For registering a selected spectrum, five optical fibers were used. Fibers where placed in parallel to horizontal plane around the flame. Each fiber was mounted on a metal ring and focused to flame center. Angle between fibers was 72°. Each fiber has a 10° field of view.

Results

Chemiluminescent intensity in the flame distributed non uniformly due to different chemical reactions occurring at different flame locations. The locations of known excited state radical

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species were determined by maximum intensity values at specific wavelengths. In all cases the maximum intensity was between 0 and 1.5 cm from burner outlet. It was found that OH* intensity at 309.8 nm has strongest intensity in all experiment result. After determination of highest intensity zones in flame a relation to excess air ratio and OH* intensity was found by interpolating experimental points with a cubic polynomial. The addition of producer gas to mixture makes chemiluminescence intensity values higher and more concentrated at distances near burner outlet. This effect is due to hydrogen presence in producer gas. OH* dependence on excess air ratio in the mixture is more sensitive to changes in air/fuel ratio. This effect might have a relation between OH* intensity ant flame adiabatic temperature, but to confirm this assumption it is important to expand experiments by adding more excess air ratio values in experiments and to implement a reliable temperature field measurement in combustion chamber. Five different measuring angles gives enough information for further analysis, by using computed flame tomography algorithms.
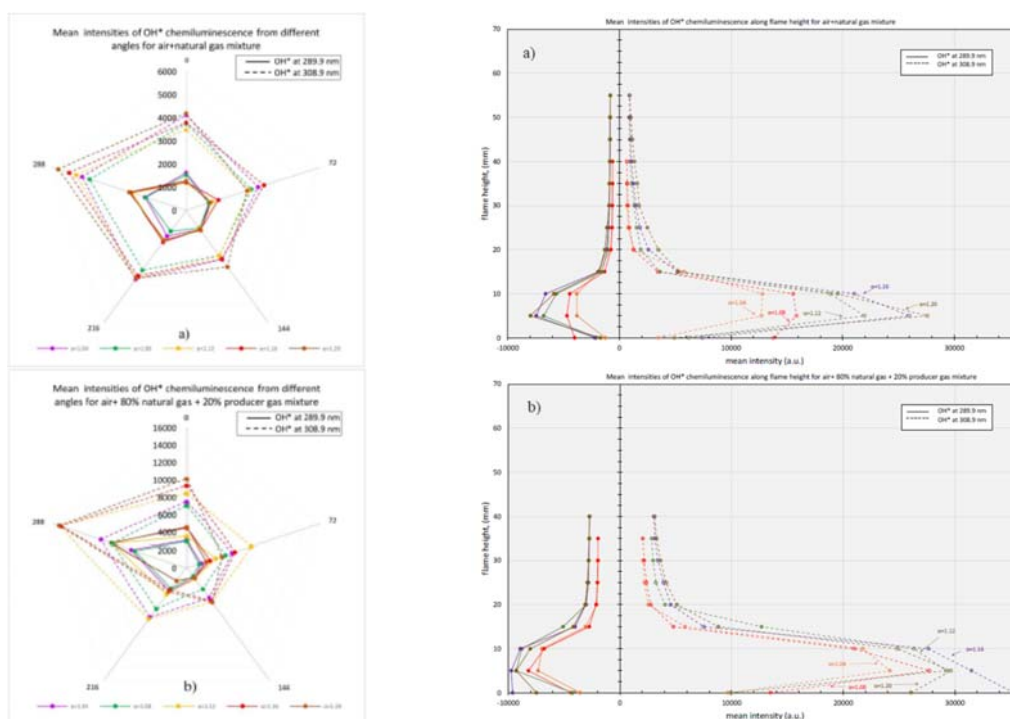

Fig. 1. Mean intensities of OH* chemiluminescence from different angles (left) and along flame height (right): a) air + natural gas; b) air + natural gas + producer gas mixture

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Uncertainties in Species Concentrations measured by Molecular Beam Mass Spectrometry

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Quantitative species data for the development and critical examination of combustion mechanisms are crucial for predictive combustion models. Mass spectrometry is one of the often-used techniques to provide mole fractions of stable and reactive intermediates including radicals from specifically designed laboratory experiments. Specifically, mass spectrometers with molecular beam sampling capacities have been coupled to premixed and counter-flow flame experiments (for example [1]) as well as jet-stirred reactors [2–4], flow reactors [5], or shock tubes [6]. The use of different ionization methods provides a powerful tool for probing combustion chemistry. Specifically, electron-ionization (EI), photoionization (PI) molecular-beam mass spectrometry (MBMS), and combinations of these techniques, have proven invaluable in numerous studies (for a detailed literature overview see [7,8]).

In order to provide precise and accurate data for model development and validation the data recording and evaluation procedure has to be done very carefully. Figure 1 shows an abstract of typical steps during the evaluation procedure of MBMS flame or reactor data. It starts with the analysis of the different recorded mass spectra [Fig. 1(a)] which includes the assignment of different mass-to-charge ratios to the respective elemental compositions and in a further step the components' identification by mass-selected photoionization efficiency (PIE) curves and ionization thresholds [Fig. 1(b)]. The species quantification, often in form of mole fraction profiles as function of burner distance or temperature [Fig. 1(c)], is the final step of the evaluation procedure. It requires an accurate calibration of the system and the measurement (or calculations) of photo- and electron ionization cross sections.
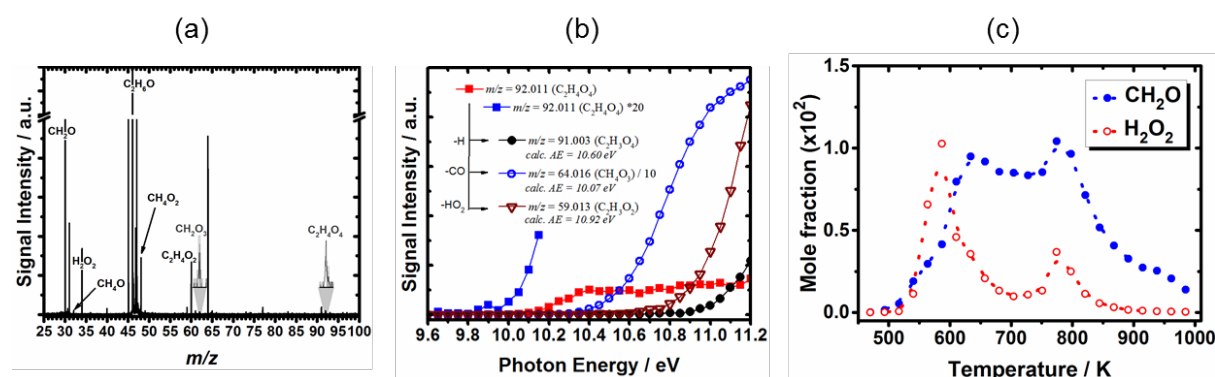

Figure 1: *Overview of different steps in the data evaluation procedure for MBMS jet-stirred reactor data: (a) the raw mass spectrum, (b) mass-selected PIE curves for the species identification, and (c) the final mole fraction profiles.*

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Each of these steps includes different sources for possible uncertainties in the final mole fraction profiles that directly influence the validation of kinetic models. Here, we present an overview of selected error sources in the data evaluation procedure of MBMS data and how they will affect the validation and development of models. It will be demonstrated how to overcome some of these uncertainties and how reliable mole fraction profiles of different species are.

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A comparative study on the oxidation of Gaseous and Liquid fuels in a swirl-stabilized flame via chemiluminescence measurements

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Background

The optimization of combustion processes is essential as emission regulations are becoming increasingly strict. In this regard, alternative oxygenated fuels such as ethanol, methanol and dimethyl ether (DME) have drawn research attention; these species appear either as fuel constituents or as additives in commercial fuel blends. In addition, modern engines employ several techniques to lower in-cylinder combustion temperatures, such as exhaust gas recirculation (EGR), hence profiting from lower NOx emissions. The introduction of oxygenates on the fuel stream alters chemical pathways and together with dilution and thermal effects which are caused by the differentiated initial charge, these shift the in-cylinder process away from traditional engine combustion. These complex interactions need to be resolved in a systematic way under controlled conditions. The swirl stabilized flame configuration considered in the present work facilitates the systematic and multi-parametric approach that is essential in order to accomplish the desired results.

Methodology

In this work, various liquid and gaseous fuels have been considered. The emission characteristics of these neat fuels have been comparatively investigated, along with the effects of an oxygenated additive (i.e. DME) and a gas mixture that contains constituents that are typically found in EGR streams. The main fuels investigated in this study were methane, propane, commercial grade propane, *n*-hexane, *n*-heptane, iso-octane and *n*-decane. Di-methyl ether and diluent gases were doped into the fuel and air streams, respectively, while keeping the thermal load of the flame constant. The experiments were carried out in an in-house designed swirl burner which has previously been described in detail [1]. Species measurements were obtained along the symmetry axis of the flame using a non-cooled Al_2O_3 probe and subsequently analyzed using a gas analyser (GA) and a gas chromatograph (GC). A ceramic insulated S-type thermocouple was used to monitor temperature. Chemiluminescence images of OH^* and CH^* were captured, helping the elucidation of flame structure behavior for different fuel types, diluents and levels of pre-heating. The same methodology has been used previously in a similar apparatus [2]. Chemiluminescence measurements provide an insight into the behavior of the flame front topology with respect to inlet condition variations and identify individual characteristics of each flame. The measured chemiluminescent species are a proxy of a fundamental combustion property; CH^* emission corresponds to the heat release zone and the flame front, while OH^* emissions define the oxidation zone.

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Discussion

This work focuses on the synergistic effects observed when adding diluent gases and dimethyl ether to commercial fuels, and also highlights the relationship between the formation of combustion intermediates and excited species luminescence. Fig.1 shows chemiluminescence signals for OH*(left) and CH*(right) for iso-octane flame configurations. Fig.1a displays a pure iso-octane flame set-up, while the addition of 10% synthetic EGR, shown in Fig.1b, reveals that the shape of the reacting flame front changes from conical to more cylindrical and the overall intensity of the flame is decreased, a finding which is in agreement with previous studies [2]. Accordingly, the luminosity of the flame front is diminished with the addition of 10% DME (Fig.1c), although the conical shape encountered in Fig.1a is maintained. As DME and EGR are supplied into the inlet mixture (Fig.1d), the reacting topology is suppressed towards the burner, resulting in a shorter and less luminous flame structure, in comparison with the benchmark pure iso-octane flame (Fig.1a). The full paper will display in detail the evolution of the flame front, emission and combustion characteristics with respect to fuel and inlet conditions.
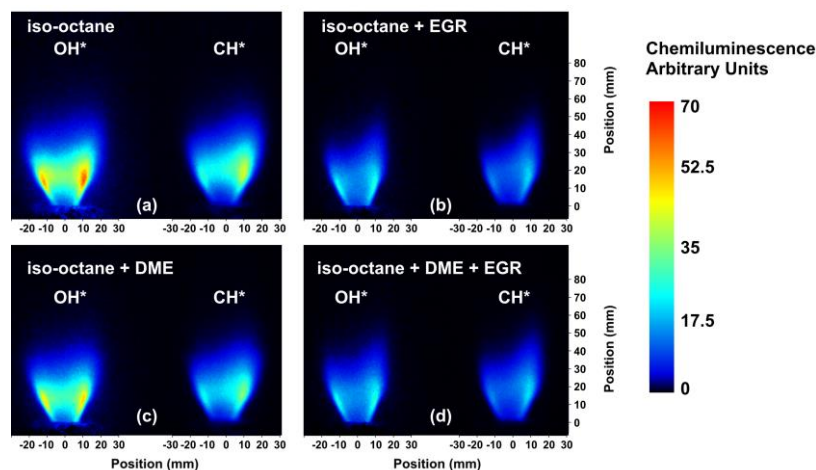

Figure 1. *Simultaneous OH* and CH* chemiluminescence images for the investigated flame configurations.*

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PCA & Kriging For Surrogate Models

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Introduction

Many engineering problems require the use of computationally expensive numerical simulations, requiring substantial computational resources. Combustion systems fall in this category, since they are characterized by very complex physical interactions, between chemistry, fluid dynamics and heat transport processes. Usually, a limited amount of resources is available and the development of reduced-order models is, thus, very appealing, in the context of optimization studies as well as for uncertainty quantification, for the prediction of the state of a complex system in a very limited time. Ideally, those reduced models should preserve the physics of the investigated phenomena, and be developed from a limited number of expensive function evaluations, i.e. CFD simulations. The combination of Principal Component Analysis (PCA) with the Kriging can be considered a promising approach in the attempt to solve this problem. Thanks to PCA, it is possible to enable the extraction of the invariant physics-related information of a combustion-related system and identify the system's coefficients which instead depend on the operating conditions. The Kriging interpolation method is then able to find a response surface for these coefficients. With this approach, a surrogate model is built that is able to perform parameter exploration with reduced computational cost. The combination of the two techniques is the focus of this work. The methodology has been applied to 1D flames, with a number of input parameters equal to 2. Variations of the classical PCA approach, namely Local and Constrained PCA [1][2], have also been employed.

Application

A data-set of 1D flames was produced with OpenSMOKE++ [3][4]. The fuel was a mixture of CH_4 and N_2. The GRI 3.0 mechanism with 53 chemical species was used. The equivalence ratio (ranging from 0.5 to 1.5 with a step of 0.05) and the molar fraction of CH_4 in the inlet (ranging from 0.4 to 1.0 with a step of 0.1) were used as input parameters. In total, 147 observations were available, 75 were used as training points, to train the reduced-order model (the sampling strategy used is described in [5]) and 72 as prediction points, for its validation.
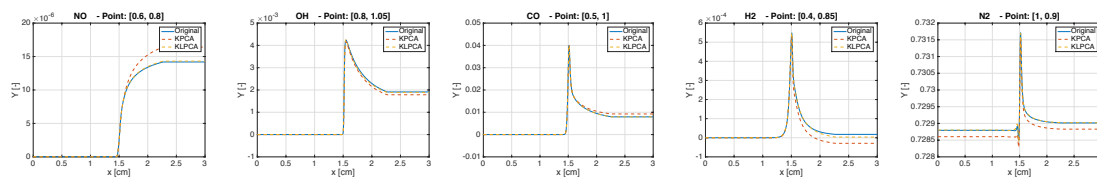
Results

Figure 1 - Prediction of the spatial profiles of the mass fraction of some chemical species (blue: original data, dashed red: PCA & Kriging, dashed yellow: LPCA & Kriging).

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The application of the methodology has produced interesting and overall positive results. In fig. 1, the spatial profiles for some chemical species predicted by the reduced-order model are reported. Usually, the implementation of Local-PCA has helped the model perform better. In fig. 2, it is possible to see that, where a measure of the error produced by the reduced-order model based on Kriging-PCA and Kriging-Local PCA is reported. The overall performance of the local formulation of the model seems to be better. Local PCA is obviously performing better at the training points, but the improvement seems to exist for the prediction points, too. Clearly, the Kriging interpolation may benefit from the clustering of the data, giving rise to a better model, even if this might not always be the case (fig. 2).
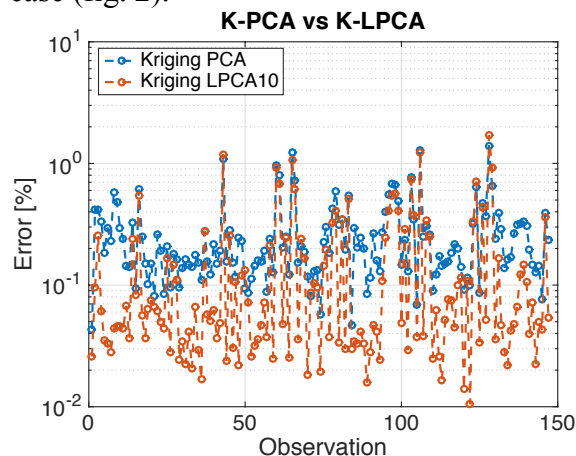

Figure 2 - Error against observations, comparison between combinations of Kriging with PCA and Local PCA with 10 clusters.

Results and further research

The results have shown that the combination of PCA with Kriging can be a valid candidate for the development of physically acceptable surrogate models that can perform accurately with reduced computational cost. Further investigation will be done on more complex systems, i.e. 2D and 3D.

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Global Uncertainty and Sensitivity Analysis of a Reduced Chemical Kinetic Mechanism of a Gasoline, *n*-butanol blend in a High Pressure Rapid Compression Machine.

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A recently developed reduced chemical kinetic mechanism describing the low temperature oxidation of n-butanol, gasoline and a gasoline/n-butanol blend is investigated using both global uncertainty and sensitivity methods with ignition delays as the predicted output for the temperature range 678 - 858 K, and an equivalence ratio of 1 at 20 bar. Firstly a gasoline surrogate is developed based on a 3 component toluene reference fuel (TRF) formulation. The study then incorporates the effects of uncertainties in forward rate constants on the predicted outputs for n-butanol, and a TRF/n-butanol blend, providing information on the robustness of the mechanism over a range of operating conditions. Uncertainty factors obtained from either both published evaluations and experimental data or from estimates made in the absence of sufficient data, were assigned to the 42 most important reactions screened out across the three fuel mixture using a brute force local sensitivity method. A global sampling technique was then further applied in the simulations in order to quantify the error (uncertainty) band of the predicted ignition delays while incorporating the uncertainties of the input rate parameters in the simulations. The predicted error bars currently existing within the TRF system while incorporating the uncertainties in the input rates, are quite large rising above an order of magnitude in the NTC region where the model's performance is weakest. The predicted distribution of ignition delays for both n-butanol and the TRF/n-butanol blend are also quite large, spanning up to about 2 orders of magnitude for the blend. However, in all cases, the experimental data points overlap fairly well with the predicted error bars indicating that reasonable values of uncertainty factors have been adopted for the key rates in the study. In addition, a variance-based global sensitivity analysis using a high dimensional model representation (HDMR) method is carried out to understand and rank the parameters responsible for the predicted uncertainties. For TRF, a total of seven reactions involving fuel + OH were identified as contributing to over 80% of the predicted error bars. The dominant reaction at lower temperatures is that of OH + toluene expressed as the reverse ($CH_3 + C_6H_5OH = C_6H_5CH_3 + OH$). This is somewhat surprising since a recent theoretical study by Seta et al. [1]suggested this to be significantly slower than the hydrogen abstraction route. Further investigation is required to understand why the H abstraction is not the dominant one based on the available version of the LLNL TRF mechanism. At higher temperatures, the contribution from the reaction $CH_3 + C_6H_5OH = C_6H_5CH_3 + OH$ diminishes considerably (disappearing at 858 K) while the H abstraction reaction from the γ site via OH for iso-octane becomes far more dominant. For predicted n-butanol + TRF ignition delay times, the n-butanol + OH hydrogen abstraction reaction from the α site is found to be the most dominant in terms of its contribution to the predicted uncertainties, despite the low blending ratio of butanol at 20%, while for predicted n-butanol ignition delay times, the chain branching pathway (α-hydroxybutyl + O_2) leading to the formation of the peroxy radical (RO_2) (α-C_4H_8OH-$1 + O_2 = C_4H_8OH$-$1O_2$) is the most dominant, being responsible for over 20 percent of the predicted uncertainties. For both the n-butanol and TRF/n-butanol system, the contribution from n-butanol + OH abstraction

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reaction from the γ site, is the most significant at higher temperatures (i.e. 858K). The Global sensitivity plots representing the first-order and second-order response between sampled input rates and predicted output are also discussed in order to explore and illustrate how the choice of a parameterization in the scheme impacts on the predicted output uncertainties. First-order functional plots for TRF indicate that modifications to the rate of fuel + OH for toluene and that of H abstraction for iso-octane from the γ site are unlikely to improve the level of agreement with the experimental data at lower temperatures, but increasing the rate of the abstraction reaction from the α site for iso-octane could lead to a decrease in reactivity and better agreement. This is however, dependent on the influence of second-order and higher-order interactions. Within the NTC region where the iso-octane H abstraction reaction by OH from the γ site dominates, better constraint is provided by the measured ignition delay data on the rate of the branching ratio for iso-octane than on the overall or individual abstraction rate for the α and γ site. For TRF + n-butanol, the overall response for the two most dominant n-butanol + OH abstraction rates (α and γ site) to the predicted delays is nonlinear and opposite to one another. While a reasonable level of constraint is provided in the individual rate of these two abstraction reactions by the measured data, as indicated by the computed sensitivities, none of them solely dominants the predicted output uncertainties.

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Investigation of the Effect of Correlated Uncertain Rate Parameters on a Model of Syngas Combustion Using a Generalized HDMR method

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Combustion models based on detailed reaction mechanisms usually have many parameters, the quantification of which involves a level of uncertainty. Uncertainty analysis is widely used in combustion chemistry [1, 2] to investigate the uncertainty of simulation results knowing the uncertainty of model parameters. A critical step in determining such predictive uncertainty is the determination of the extent of uncertainty in model input parameters. One possibility for the assessment of input uncertainties is the investigation of the parameters one-by-one by tracing the source of the parameter value. A measurement that aims to determine a kinetic or thermodynamic parameter is usually called a direct one. The evaluation of the systematic and statistical errors of these direct measurements allows an estimation of the uncertainty of each parameter [3]. In most uncertainty analysis studies carried out so far in combustion chemistry (see e.g. [4-9]), the model parameters were considered to be uncorrelated, since no information was available on their joint distributions.

Indirect measurements can be interpreted only by multi-parameter models. In combustion, such indirect measurements include determinations of laminar burning velocities, species concentration profiles or ignition delay times. Rate parameters of combustion mechanisms are intrinsically correlated, since the mechanisms are developed not only based on direct measurements, but also to reproduce the results of indirect measurements. Traditional methods for mechanism development inevitably involve some tuning of parameters within their suggested uncertainty limits, in order to reproduce indirect measurements over selected sets of conditions. This approach however, does not provide information on the correlation of rate parameters. An alternative approach is the systematic optimization of reaction mechanisms (see e.g. [10-13]), where the highly sensitive model parameters are fitted to experimental data. Such methods can provide information on parameter correlations. For example, Sheen and Wang calculated the covariance matrix of the fitted parameters for ethylene and n-heptane combustion mechanisms [14-16], which carried information on the joint uncertainty of the parameters. The optimized rate parameters were Arrhenius A parameters and 3rd body collision efficiency factors. Turányi et al. [17-20] extended the methodology to the determination of all Arrhenius parameters A, n, E of important reaction steps together with the fitting of the important 3rd body collision efficiency factors. They also calculated the covariance matrix of all determined parameters. It is expected that the joint uncertainty of model input parameters will be available for more and more combustion systems as optimization methods become more widespread. Therefore, development of global uncertainty and sensitivity analysis techniques is needed that can utilize the newly available, more realistic correlated uncertainty of the parameters.

The High Dimensional Model Representation (HDMR) method has been applied in several previous studies to obtain global sensitivity indices of uncorrelated model parameters in combustion systems. However, the rate parameters of combustion models are intrinsically correlated and therefore uncertainty analysis methods are needed that can

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handle such parameters. A generalization of the HDMR method is presented here, which uses the Rosenblatt transformation on a correlated model parameter sample to obtain a sample of independent parameters. The method provides a full set of both correlated and marginal sensitivity indices. The accuracy of the methodology was tested on simple test cases. Also, ignition delay times predicted by an optimized syngas–air combustion model were investigated using this new global sensitivity analysis tool. In the case of the ignition delays, the sensitivity indices which account for all correlated effects of the rate parameters are shown to dominate uncertainties in the model output. However, these correlated indices mask the individual influence of parameters. Although the uncorrelated indices are small, they provide insights into the dominant chemical and physical processes of the model at the conditions studied. The implications of this result on model development are discussed.

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An Open Science Cloud for Molecular Science Services

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PREAMBLE

Molecular science is dramatically changing the way of producing and using knowledge. Modern information and communication technologies have in fact progressed to the point of offering unprecedented access to data sources, efficient data analysers and simulation facilities. Open science leverages on this technological evolution to the end of making easily accessible research services, information reuse, commercial and societal exploitation of innovative processes. In the past the molecular science community moved towards the Open Molecular science by establishing the Virtual Organization (VO) COMPCHEM (https://www.egi.eu/community/vos/) and a Virtual Research Community (VRC) CMMST (https://wiki.egi.eu/wiki/VT_Towards_a_CMMST_VRC) within the activities of the European Grid Infrastructure (EGI). This has fostered hardware and software sharing as well as applications composition in workflows and meta-workflows as is the case of the Grid Empowered Molecular Simulator (GEMS) [1] that coordinates the use of the state-of-the-art from first principle electronic structure and nuclei dynamics calculations to simulate the measurable properties of reactive scattering.

THE PROJECT

A significant fraction of the COMPCHEM VO [2] and of the CMMST VRC [3] laboratories have now gathered into an Open Molecular Science project targeting a bottom up implementation of the collaborative distributed Research Infrastructure (RI) designed in the SUMO-CHEM proposal. That proposal (n. 731010-1), submitted to the Horizon 2020 framework call H2020-INFRAIA-2016-2017 (Integrating and opening research infrastructures of European interest) was not funded [4] in spite of being evaluated positively for the idea of connecting experimental and computational chemistry communities and infrastructures, for the capacity of going beyond the state-of-the-art, for the proper selection of use cases and for its activities in multidisciplinary and development of networking.

THE CONTRIBUTION OF THE PERUGIA GROUP

For this purpose the Perugia group is developing a B2cmmst (Business to CMMST) service in which a Molecular Science Cloud for running community specific applications is being implemented. The service is aimed at orchestrating the activities of both the e-infrastructure experts and the Molecular and Materials researchers so as to enable an effective intra- and trans-community networked implementation and coordination of collaborative/competitive applications.
The service is aimed at allowing both:
- a discovery of the computing resources and their quality selection and automated access,
- the access to a software list and the coordinated usage of distributed software,
- the use of specialized web portals and the production and reuse of data and know how,
- the monitoring of collaborative activities and their reward.

To this end the Perugia group is going to deploy, and if it is the case maintain, small/medium sized virtual high performance computational clusters, remotely managed on virtualized platforms, configured for molecular science research activities. The virtual cluster appliance implements a scalable linux x86_64 homogeneous cluster managed by a batch parallel system (Torque/Maui) with ready to use compilers, linear algebra numerical parallel libraries (BLAS, LAPACK, ScaLAPACK), message passing libraries (mpich, mvapich2) and a basic suite of molecular science applications tested by experienced users. The technology proposed relies on the definition on the user side of an environment enabling cloud implementations. The prototype environment already implemented includes a 64bit, x86_64, FE-Cluster platform for production runs, a 32bit, i686, CG-Cluster platform for educational purposes and it is also going to include a 2 GPU based machine.

The cloud environment will be developed using OPENSTACK (in collaboration with the local INFN section) in which storage sharing between chemistry and physics infrastructures will be guaranteed by a dedicated connection. The service has been developed over the last two years, in the context of an internal project named Herla [5].

THE DEMO APPLICATIONS

The demo application will consist of a dedicated use of GEMS to the study of some combustion relevant processes: a specific use case has been devoted to increase our understanding of combustion processes and carbon efficiency in energy production[6]. Another use case based on GEMS is a complex kinetic system involving heterogeneously catalyzed processes whose efficiency parameters are derived from ab initio studies, checked against highly detailed measurements of the corresponding elementary gas phase processes obtained from molecular beam-beam and beam gas experiments. The measurements will also utilize a prototype industrial apparatus[7], built by a consortium of SMEs coordinated by the Perugia University spinoff Master-up srl, to use energy from renewable sources to produce methane from CO_2 and store it in forms easy and safe to transport. The accurate calculations of the dynamical properties will make use of both time dependent and time independent techniques and related packages. GEMS will be also used for investigating plasmas in non-equilibrium conditions[8].

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Controllability and reachability of reactions

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Introduction

In many areas of chemistry one has to achieve a certain goal: to maximize the yield, to minimize the dangerous materials escaping to the environment, to acquire an appropriate dosing of a drug, etc. All these problems can be formulated as a control problem. A key issue in control theory is the controllability of systems [1,2,3]. Here we investigate the controllability of chemical reactions.

Controllability and reachability

There are many different controllability definitions in the literature. The most common controllability properties are: reachability, strong reachability, local controllability, small-time local controllability and global controllability. A system is reachable from an initial state if the set of states where the system can get with all the admissible inputs (called reachability set) at some fixed time has an interior point. If this set has an interior point for all fixed times, then the system is said to be strongly reachable. The system is locally controllable, if the initial state is the interior point of this set for some time, and the system is small-time locally controllable if the initial state is the interior point of the reachability set for arbitrary small time. The system is globally controllable, if for all initial states, the reachability set is the whole domain of the system.

Our previous analysis [1] showed that chemical reactions are usually not locally controllable, but strongly reachable. This reflects the phenomena that the concentration of certain species can only be decreased or increased in some reactions, so we can not get back to the initial state, thus the system can not be locally or globally controllable, but can be reachable. However, since in most situation the goal is to increase the concentration of the product species, it is not a problem that the system is only strongly reachable.

Using reaction rate constants as control inputs

The control inputs of a chemical reaction considered as a control system can be: the reaction rates of the reaction steps, the temperature of the environment, the concentration of some species participating in the reaction, etc. In [1] and [2], the analysis have been done with control systems whose control inputs were the reaction rates of the reaction steps. In [2], it was shown that if all the reaction rates are control inputs, and the system has a positive equilibrium, then the system is locally controllable in that equilibrium. We showed in [1] that if all the reaction rates are control inputs, then the system is locally controllable in every point of the positive orthant, i.e. for all positive concentration values. Controllability analysis requires the examination of the Lie-algebra generated by the vector fields corresponding to the different inputs of the system. Since all the reaction rates are control inputs, all the vector fields in the differential equation of the reaction correspond to some inputs; such a system is called a driftless system. However, if not all

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the reaction rates are used as control inputs, there will be some vector fields that cannot be directly affected by the inputs, the sum of these vector fields is called the drift vector field, and the system is said to have a drift. If the system has a drift, then we cannot conclude local controllability from the generated Lie-algebra, only strong reachability.

We have defined critical reaction steps [1] whose reaction rates need to be control inputs in order to get a strongly reachable system. We have defined the initializer reaction steps, whose species in its reactant complex do not participate in other reaction steps, except if they are catalysts in the other reaction steps. We have proved that initializer reaction steps are critical reaction steps as well. We have also defined initializer classes that are sets of reaction steps whose linear combination is an initializer, and proved that each initializer class has at least one, not necessarily unique critical reaction step.

Identifying the initializer reaction steps and the initializer classes can help us to drastically decrease the number of necessary control inputs, in an extreme case, for consecutive reactions (as defined in [1]) it is enough to have one control input. The other extreme is the Robertson-model that is only controllable if all the reaction rates are control inputs.

Controllability and reachability with positive inputs

The analysis based on the Lie-algebra generated by the vector fields defining the differential equation of the system is based on the examination of the dimension of a linear subspace, i.e. linear combinations of vector fields, whose coefficients are basically the control inputs. This also requires that the control inputs can have any real values. However, in general control inputs are (strictly) positive, meaning that subspace based methods may fail to give proper results. For example, the analysis with all reaction rates as control inputs showed that the system is locally controllable in every point of the positive orthant, however it may not be true if the control inputs can only be positive. This problem can be investigated by extending the original differential equations of the system by adding a differential equation for each input that guarantees positivity, however in this case the system will have a drift, and we can only investigate strong reachability. Thus, if the inputs can only be positive, local controllability results become only strong reachability results.

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ChemConnect2016:

Interconnected Network of Combustion Data

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ChemConnect2106 is a combustion database, derived from mechanistic, kinetic and thermodynamic data, organized into a network of interconnecting concepts. This differs from traditional databases in that the published data, for example from detailed mechanisms, is broken down into fine-grained data, meaning individual kinetic, thermodynamic and structural constants, and this constants are interconnected through relationships. For example, a species label is connected to a reaction through the relationship saying that it is a product of (*ProductOf*) that reaction. The principle is based on the *Resource Description Framework (RDF)* from the World Wide Web Consortium's (W3C) semantic web specifications.

The focus of the initial phase is to extract fine-grained information from published (combustion) data sets. These relationships form an expansive network of inter-connected keywords and concepts. Searching within the database is keyword based and entails traversing the network of these relationships. Using this representational paradigm, two networks created independently from different data sources become naturally intertwined through their common keywords and concepts. ***ChemConnect2016*** is part of the larger *Very Open Data Project* whose goal is to create flexible and dynamic platform for the management of scientific information (current focus, the combustion community).

The three main sources of information within the database now are published mechanism (CHEMKIN formatted)s found on public repositories, published thermodynamic data (in NASA polynomial form) and some of the 2D-graphical information (structural, kinetic and thermodynamic) from automatic reaction generation systems (REACTION, THERGAS/JTHERGAS). Fine-grained information, meaning, for example, individual constants, labels and structures are extracted from these sources and the database network of relationships is built.

Searching the database: User point of view

The basis of the search is the use of keywords. These keywords can be species labels, isomer expressions, reaction expressions, source names, and specific reference keywords. The database is searched for these keywords and related data, and how it is related, is given. The related data can be individual pieces of information, in the form of a keyword, or, if it exists, a complete data object. If a result is a keyword, that keyword can be searched (by clicking it) to find further related information. In this way the user wanders through the network of related data to find the specific information being searched for.

For example, if one enters a species label name, several pieces of information can arise: the species as it appears in published data, such as a mechanism (the mechanism name is appended to the name to distinguish how this species label is used in that particular

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mechanism), the canonical isomer name, the reactions in which that species label is used, and 2D-species data using that species label. The user can then click any of these pieces of information to explore the database further.

In an example of exploring the database further, maybe the species label given does not match a name used in other mechanisms. This information can be found by clicking the related isomer keyword. This will give all the specific species labels in each mechanism in which this isomer exists. Some of these labels could be the result of a different labelling of the mechanism developer or actually a different structural isomer.

If a specific, mechanism related, species label is clicked, then the user can explore how this species reacts within the mechanism, as a product or as a reactant along with the specific reaction constant information, thermodynamic information and even transport data, if given. By exploring the reaction further, the user can compare the rate constants used in each of the mechanisms.

Data Relations

The key to creating this network of chemical information is the establishment of individual relationships. A relationship has the following form:

subject (keyword)   —> Relationship —> object (keyword or data structure)

The *subject* is an individual keyword, such as a species name or even a reaction (in canonical form). The *object* in this relationship, which can be another keyword or a more a data structure of information. The *relationship* is how the object and the subject are related. An example relating a species name to an isomer keyword could be:

ic3h5chcoch3 —> isIsomerOf —> c6h9o

This relationship represents one link in the network and connects to other pieces of data if the object or subject keywords match. Though the isomer relation, the isomers ic3h5chcoch3 and ic4h7coch2 are linked.

*ic3h5chcoch3 —> isIsomerOf —> **c6h9o** <— isIsomerOf <— ic4h7coch2*

Information between mechanisms, in this case a mechanism from LLNL (PRF) and a mechanism from Princeton (nC7H16), can be linked through the same species label:

LLNL#PRF —> MechSpecies—> LLNL#PRF#ic3h5chcoch3 —> Species —>
ic3h5chcoch3
<— Species <— Princeton#nC7H16#ic3h5chcoch3 <—Mechpecies<—Princeton#nC7H16_red52

Connecting information between datasets

One sees from the example of the previous section, independent data sets can be linked and compared. A fundamental advantage to using relationships is found in the second example. Namely, no specific reference between the mechanisms is found in the raw data from which the relationships were formed. It is only through the building of the relationships that a connection is found. This property gives an enormous dynamic and flexibility to the database.

The concepts of **ChemConnect2016** will be explained during the prevention and demonstrated during the workshop. Users will be tutored in hands-on usage of the database.

REDUCED CHEMICAL KINETIC MECHANISM FOR PRFs

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Introduction

Common fuels (gasoline, diesel, natural gas, ethanol, etc.) used in most of the vehicles are mixtures of hydrocarbons, consisting of hydrogen and carbon atoms. In a "perfect" combustion, oxygen reacts with the hydrogen in fuel to form water and all of the carbon turns to carbon dioxide. However, since the combustion process is not "perfect", automotive engines causes several types of pollutants such as hydrocarbons, nitrogen oxides, carbon monoxide and carbon dioxide. As a result of incomplete combustion process these exhaust emissions pollute the air considerably [1,2].

Today, chemical kinetic modeling is extensively utilized to develop the combustion process in ICEs and optimize them. However, detailed chemical kinetics mechanisms are needed to fully understand the combustion process. However, the computational cost of detailed chemical kinetics is beyond the capacity of current computers to simulate an actual combustion process in a reasonable time. Therefore, it is necessary to make some simplifications. The most common technique used to solve this problem is the reduction mechanism that is derived from detailed chemical kinetics [1-4]. Thus, it is possible to obtain accurate results using less computing resources.

In this study, a PRF mechanism consisting of 1034 species and 4236 reactions was reduced into a mechanism consisting of 70 species and 295 reactions using the reduction methods which are DRGEP, DRG, DRGEPSA, DRGASA, CSP-QSSA and FSSA as seen in Table 1 and the comparison of these reduction methods is only carried out in terms of the first step reduction (Table 2). The accuracy of the reduced mechanisms are provided to compare with the detail mechanism in terms of pressure, temperature, heat release rate (HRR) and emissions, (Figure 1). The analyses were made for an HCCI Engine [5] with initial conditions: p_o=1.0 bar, T_o=393 K, φ = 0.2857. Engine speed is set to 900 rpm. Compression ratio and displacement volume are 16.7, 1.95 dm^3, respectively. Reduced mechanisms are only valid under the pre-defined conditions.

Results

The results have been shown that the reduced mechanisms are compatible with the detail mechanism for both convergence and trace of the detail mechanism and errors are in acceptable limits. However, there is a bit deflection to follow the curve of the detailed mechanism at FSSI reduced methods.

Table 1. *Skeletal and optimum reduced mechanisms*

DETAILED	1034 species 4236 reaction
DRGEP	183 species 800 reaction
DRG	175 species 732 reaction
DRGEPSA	175 species 732 reaction
DRGASA	156 species 649 reaction
CSP-QSSA	141 species 615 reaction
FSSA	**70 species 295 reaction**

Table 2. *The comparison of various reduction methods in terms of the first step reduction*

Size of reduced mechanism	Cost	Method
208 species 836 reaction	6 min.	DRG
183 species 800 reaction	6 min.	DRGEP
200 species 781 reaction	10 min.	DRGASA
180 species 777 reaction	7 min.	DRGEPSA
464 species 2239 reaction	7 hour 23 min.	CSP-QSSA
199 species 556 reaction	15 hour 27 min.	FSSA

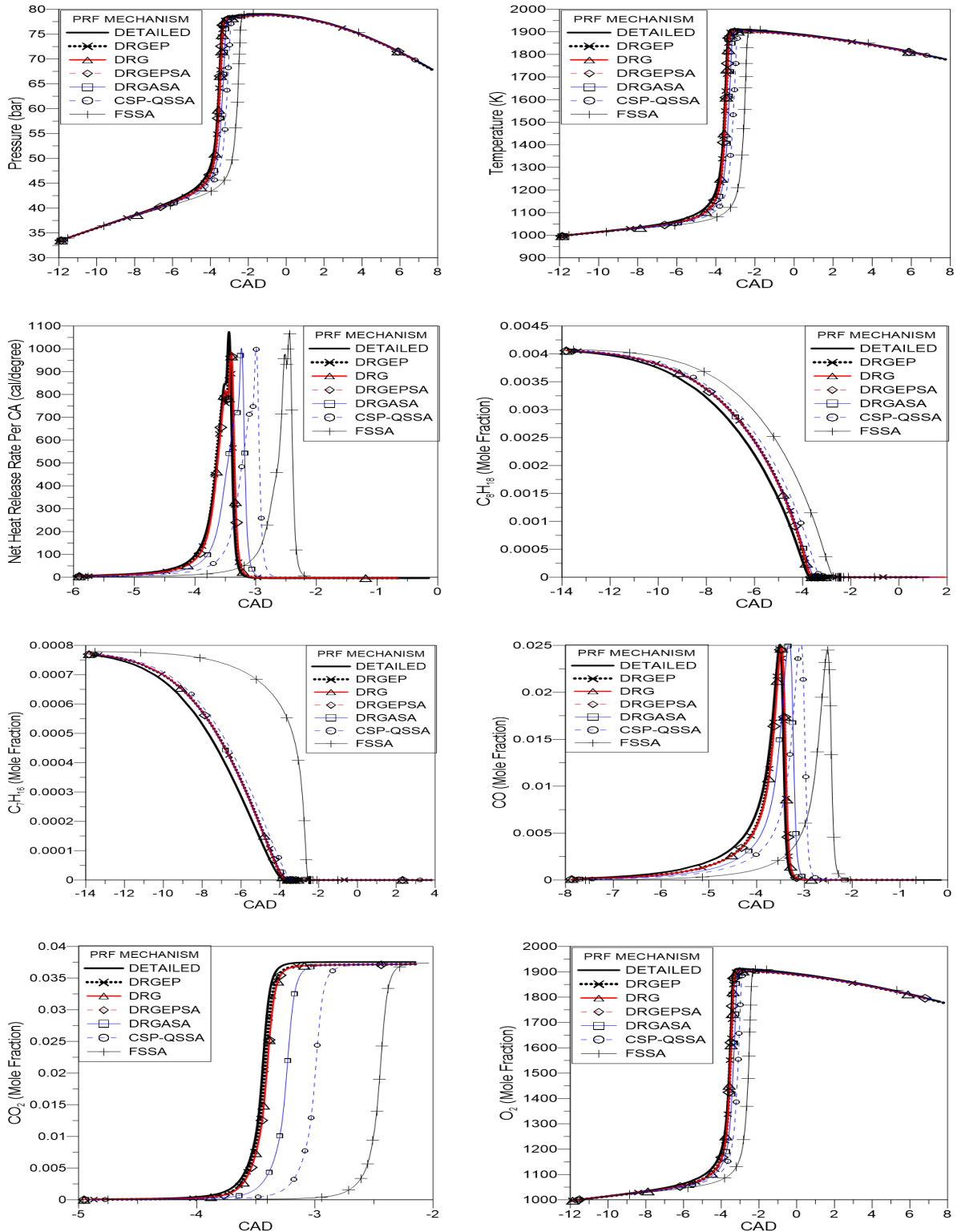*corresponding author*: Hakan Serhad SOYHAN, hsoyhan@sakarya.edu.tr

Fig. 1. *The comparison with the detailed mechanism of the optimum reduced mechanism*

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Towards a fully automated system to develop, validate and evaluate combustion kinetic mechanisms

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Abstract
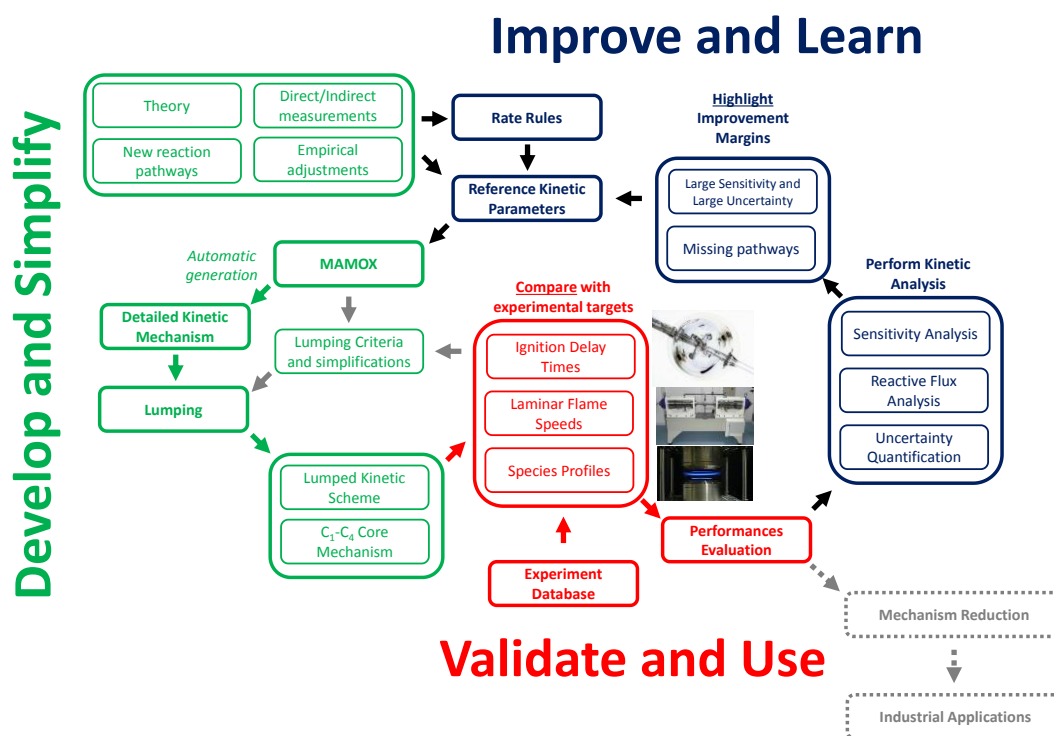
Figure 1: Flow chart of the development, validation and improvement process of the POLIMI kinetic mechanism.

The increasing number of experimental data, accurate thermodynamic and reaction rate parameters drive the extension, revision, and update of large size kinetic mechanisms.

The complications related to the manual construction of these models in terms of number of species ($\sim 10^2$-10^3) and reactions ($\sim 10^3$-10^4) have been already bypassed through the definition of reaction classes and rate rules defined on the basis of a limited number of intrinsic kinetic parameters [1-3]. This systematic approach facilitated the implementation of computer-based expert systems for the automatic generation of kinetic mechanisms [4, 5] which have been widely used by the kinetic community in the last ~30-40 years [1]. Other simplification techniques such as lumping of species allow to keep the size of kinetic mechanisms to a reasonable level.

Despite these detailed mechanisms generally allow good predictive capabilities, their management and update are critical. Reasons for such criticism are quite well understood. On one side the

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outstanding progresses of theoretical chemistry [6] suggest the update of kinetic and thermodynamic parameters for both small species belonging to the core C_0-C_3 mechanism and for larger fuels [7]. While the latter might have a more limited impact, the perturbation of small species chemistry strongly propagates its effect throughout the whole mechanism. On the other side the increasing number and accuracy of experimental measurements makes the validation procedure, commonly performed over the widest range of conditions, challenging and time-consuming. Beside the computational time (e.g. laminar flame speed), another time-consuming part is the unrealistic option of graphically comparing every data set with an enormous number of kinetic simulations in ideal reactors. The challenge in the validation procedure is twofold. Firstly the substitution of the rather subjective *good* or *bad agreement* statement with a more quantitative and general evaluation is a mandatory goal of the modern kinetic modelling efforts. Some first important step has been recently reported in the literature with the work of Olm et al. [8] and Bernardi et al. [9]. The second key aspect is the definition of a general, efficient and, most importantly, shared format to instruct a database where storing our targets, and, to some extent our knowledge of reality. Efforts in such direction are already available in the literature [10-15] and time has come to put pieces together and seek for a common goal.

If properly stored such information can allow a full automation of the validation process by linking the experimental database, to a standard kinetic solver such as OpenSMOKE++ [13] and to the Curve Matching framework [9] to iteratively assess the validity of the mechanism.

This procedure is summarized in the red portion of Figure 1 and progresses in such direction are presented in this work.

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Methane Oxidation over Doped Nickel Catalysts under Reforming Conditions: A DFT Study

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The growing surplus of natural gas creates new possibilities for production of high value, sustainable and environmentally friendly fuels and chemicals, such as syngas and synthetic fuels. Methane (CH_4) is a potent greenhouse gas (GHG) with a global warming potential significantly higher than that of carbon dioxide. However, complete conversion of methane in the gas phase is challenging, mainly due to its high relative stability, requiring high temperatures and resulting in significant noxious emissions. Catalytic combustion/partial oxidation of methane offers significant advantages. Dry reforming (DRM) or steam-assisted dry reforming (SADRM) of methane, in particular, utilizing two abundant GHG can lead to reduced carbon emissions particularly if combined with solar heating to drive the endothermic reaction.

Developing efficient non-noble metal catalysts for methane reforming processes is a challenging task. In this work the effect of different alloying additions on the coke deposition resistance and activity of the nickel catalyst was numerically investigated using Density Functional Theory. Silicon, Zn, Fe, Co, Mo, Sn W, and W combined with Zn were selected as dopants to the Ni(111) surface. The CH_4 and H_2O dissociation were taken into account and two main pathways were studied; the C and CH oxidation. The carbon diffusion into the subsurface of the catalyst was also investigated. The adsorption energies, reaction enthalpies, transition state geometries and energy profiles of the overall reaction process were calculated and found to be in good agreement with literature data. A high CO dissociation barrier was found for all surfaces under study, making carbon deposition from CO dissociation highly improbable. It was also found that C diffusion into the subsurface of the catalyst is an exothermic reaction regardless of the dopants introduced to its surface. Tin, Zn and W/Zn doped surfaces exhibit the smallest C to CH oxidation barrier ratio and the largest effective barrier difference between C and CH oxidation pathways which would indicate that Sn, Zn and the combination of W and Zn may be used to reduce the carbon deposition on the nickel catalyst surface. The Zn and W/Zn doped surfaces showed the strongest binding with the adsorbate species and that their synergetic effect on the catalyst activity was significantly beneficial, as their combination would lead to significantly lower activation barriers than that on the pure nickel surface.

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Development and Validation of Detailed Chemical Kinetic Mechanisms for the Prediction of NO_x-SO_x Synergies

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The increased environmental interest for reducing pollutant emissions from the marine industry has forced the IMO and national authorities to set strict emission control regulations in specific geographical areas (Emission Control Areas - ECAs), with emphasis on nitric and sulfur oxides (NO_x, SO_x). The prediction of NO_x and SO_x emissions from large marine Diesel engines requires the coupling of CFD tools with realistic (skeletal or reduced) chemical kinetic mechanism. This in turn requires the development of reliable detailed kinetic mechanisms capable of accurately capturing the interactions in the H/C/O/N/S system. In the present work validated detailed hydrocarbon chemical kinetic mechanisms have been coupled with NO_x and SO_x sub-mechanisms and evaluated against experimental data relating to the oxidation of CO-H_2 and CH_4 mixtures. Results are presented for the oxidation of CO-H_2 and CH_4 mixtures in a jet stirred reactor at atmospheric pressure, for several equivalence ratios (i.e. φ: 0.1, 1.0, 2.0 for the CO-H_2 mixtures and φ: 0.1, 0.5 for the CH_4 mixtures) and for initial concentrations of NO and SO_2 in the order of 0-5000 ppm [1, 2]. Simulations have been performed using the GRI3.0 mechanism [3] and the C1-C3 version of the CRECK mechanism [4]. The resulting mechanisms are referred to as GRI3.0+ and CRECK+ respectively. In both cases the SO_x sub-mechanism and the N/S species interactions from the work of Glarborg and co-workers [5, 6] have been used. Typical results are shown in Figs. 1 and 2.
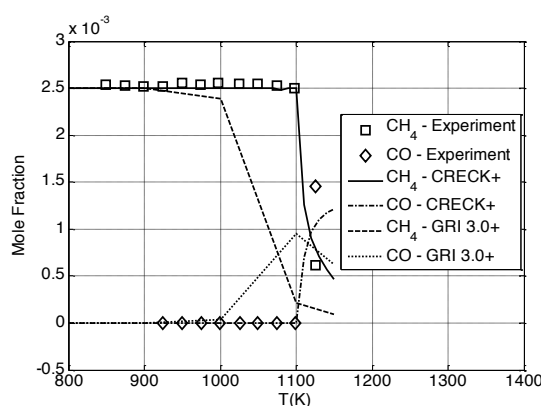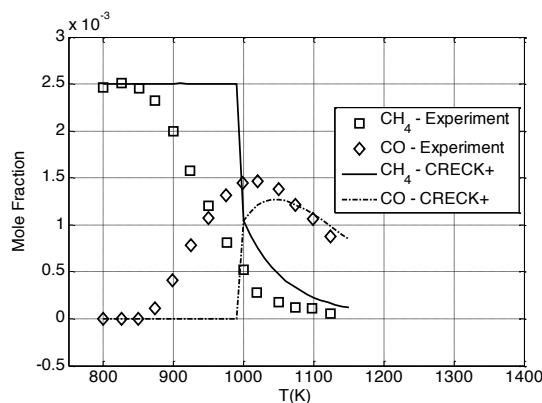

Fig. 1 *Comparison between experimental [4] and simulated CO and CH_4 profiles for the oxidation of CH_4 in a JSR at φ=0.1, P=1 atm.*

Results yield a solid basis for comprehensive understanding of the effects and synergies between NO_x and SO_x on hydrocarbon oxidation. Specifically, it is shown that mechanisms generally fail to capture methane or syngas ignition for low temperature (<900K) while at high temperatures (e.g. >1100K) the performance of CRECK+ is very satisfactory. The performance of GRI3.0+ is generally poor. The present study clearly

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indicates that the existence of trace quantities of NO in the mixtures tend to significantly accelerate the overall reaction. The addition of trace quantities of SO_2 does not have such a drastic effect, however it markedly deteriorates the quality of agreement between numerical experiment and simulation. Modifications in the N/S sub-mechanism are proposed and assessed on the basis of the experimental data. The present work constitutes the first step towards the development of an optimized detailed chemical kinetic mechanism. This in turn, will provide the basis for the development of appropriate reduced schemes for realistic CFD studies of NOx and SOx in large marine engines.

Fig. 2 *Comparison between experimental [4] and simulated CO and CH$_4$ profiles for the oxidation of CH$_4$ in a JSR at φ=0.1, P=1 atm with the addition of 220ppm NO.*

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Acknowledgements

Conceptual approach for determination of baseline and target values of air quality indicators

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Motivation

The Priority axes 5 (PA 5) of the Bulgarian Operational Programme Environment 2014-2020 (OPE) [1] aims at improving the ambient air quality by reducing the quantities of particulate matter (PM_{10}) and NO_X. In the process of negotiations with the European Commission (EC), actions to be undertaken to fulfil ex-ante conditionalities under OPE with the respective deadlines are agreed. One of these conditionalities requires the existence of a system of result indicators necessary *to select actions, which most effectively contribute to the desired results*, *to monitor progress towards results* and *to undertake impact evaluation*.

Objective

The *specific objective of PA 5 of the OPE* is to *reduce the ambient air pollution by lowering the quantities of PM_{10} and NO_X.*
The respected *result indicators* for this PA are defined in the text of the programme as *the quantity of PM_{10} and NO_X* (in terms of *NO_2) in the ambient air in tonnes per year (t/y)*, which is appropriate to be described by the *emissions* of the appointed substances.
Thus, the goal of the present work was to develop a concept for a quantitative approach allowing to determine the so called *baseline* (*BV*) and *target values* (*TV*) of the result indicators.

Concept development

The currently developed concept aims at proposing methodological approach for calculating the BV and the TV of the result indicators under PA 5 of the OPE; as well as for the establishment of a procedure for processing the existing data, and for collecting new data at the occurrence of a need, related to the estimation of the BV and TV of the respective indicators.
This methodological approach should be in line with the emission inventory of the key sectors/categories/sources of pollutants and their share contribution to the total level of air pollution for a certain period, according to the Updated Unified Methodology for Inventory of the Emissions of Hazardous Substances into the Air [2]. The methodology from [2] is developed in conformity with the Air Pollutant Emission Inventory Guidebook of the European Monitoring and Evaluation Programme and the European Environment Agency for 2009 (EMEP/EEA air pollutant emission inventory guidebook [3]), which updated edition from 2013 is available at [4].
The concept can be expressed in terms of two major stages, as follows:
- **Stage I:** Estimation of the BV;
- **Stage II:** Estimation of the TV of the result indicators.

The main activities planned in the prescribed procedure for implementation of *stages I* and *II* are schematically described in **Figure 1**, in a logical sequence.

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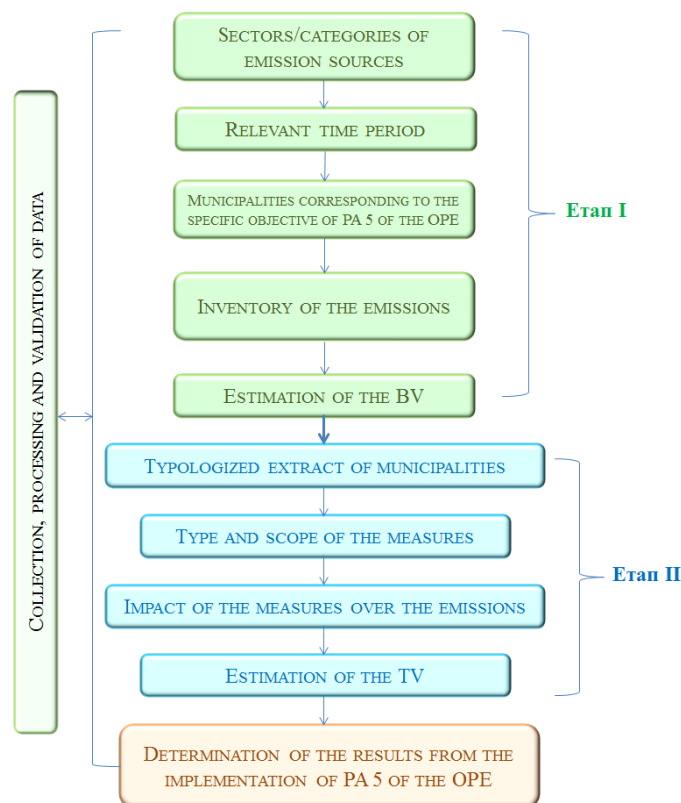
Figure 1: Procedure for estimation of BV and TV of the result indicators under PA 5 of OPE

The current methodology is still work in progress. The work is being conducted in the frame of national and international collaboration initiatives, assuring the successful elaboration of its complete version, and its final approval.

Acknowledgment

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Flame stabilization in high velocity ratio plane coaxial and convoluted trailing edge nozzles.

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The work presents a comparative study of the fuel-air mixing and flame stabilization characteristics of two, high velocity ratio, coaxial jet configurations comprising either a plain circular (PC) arrangement or a convoluted trailing edge (CTE) nozzle (Figure 1). The high velocity ratio, coaxial stream interaction results in a stable central recirculation zone at a distance downstream of the nozzle exit where a range of flame configurations can be successfully stabilized under suitable flow and mixing conditions. In this configuration, the reacting front region is supplied with both a radial (Figure 2) and an axial (Figure 3) propane-air mixture gradient which are achieved through a central upstream premixer duct and the co-annular jet interaction downstream of the exit plane. Depending on the examined nozzle shape, plain circular or convoluted, a variety of partially premixed turbulent flame configurations can be obtained at a position detached further from the nozzle exit. Measurements of mixture concentrations, mean temperatures, and flame chemiluminescence images of OH* and CH* provided information for the interpretation of the relative variations in flame structure and burner performance. Preliminary supporting computational investigations for the cold flow fuel-air mixing patterns and the accompanying mixing wake axial velocities have also been conducted to give an insight into the predominant aerodynamic phenomena involved. The combined methodology helped to elucidate some aspects of the influence of the variable inlet fuel-air mixture distributions and their interaction with the high velocity ratio co-axial jet mixing topologies on the diverse flame configurations studied.
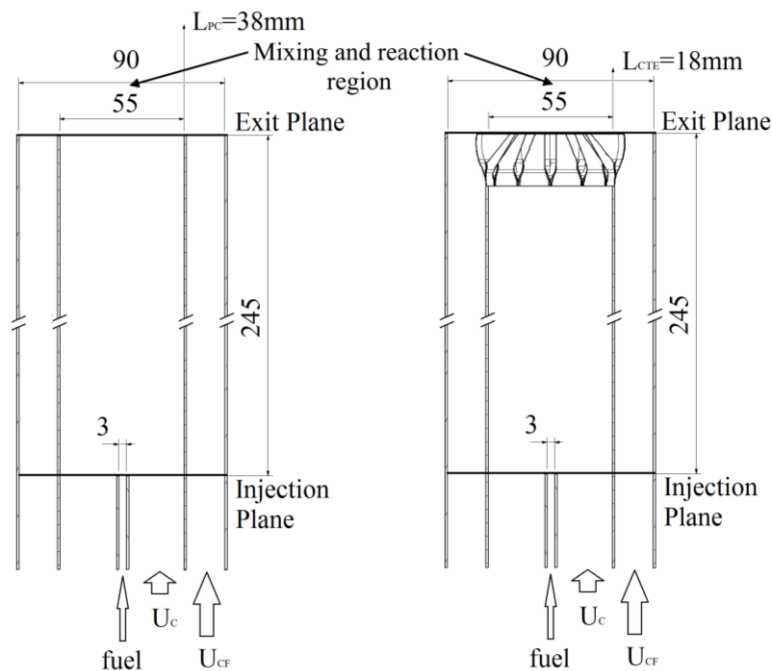

Figure 1. Experimental configurations and co-annular mixing nozzle geometries.

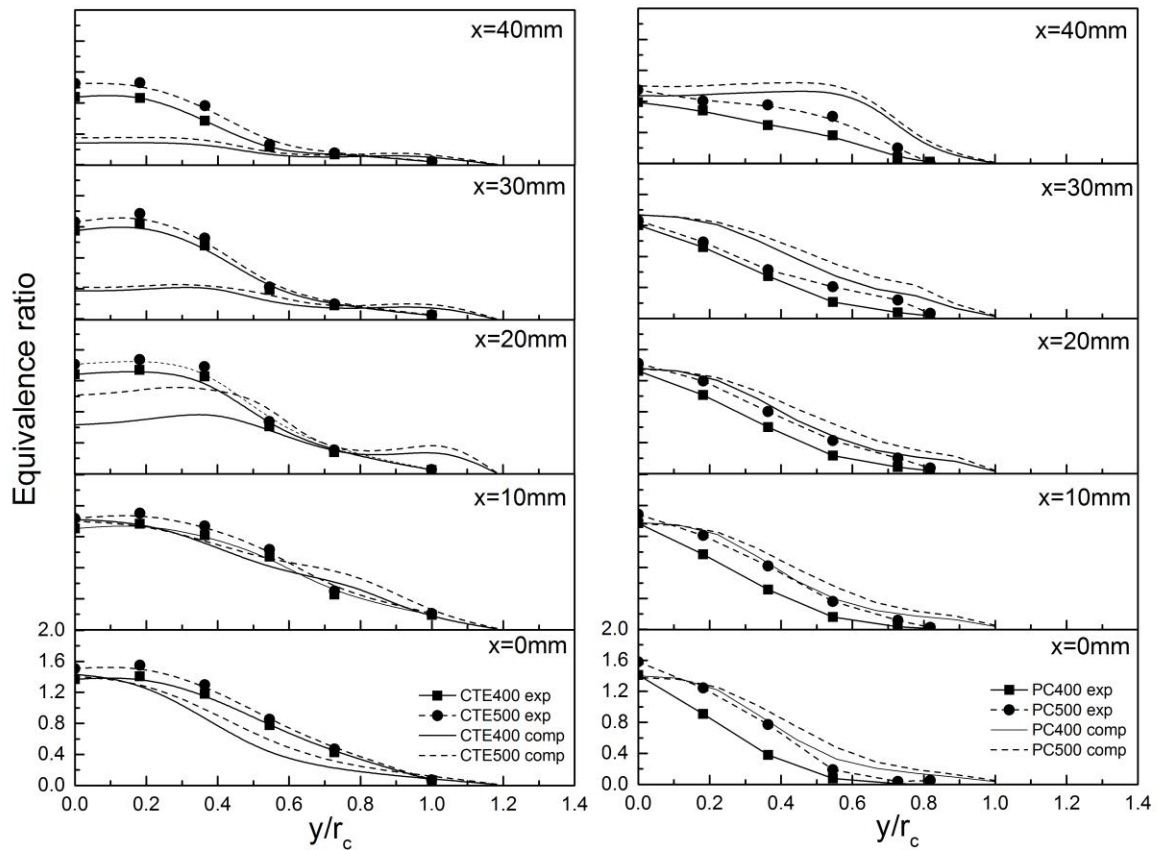*corresponding author*: Souflas Konstantinos e-mail:souflaskonstantinos@gmail.com

Figure 2. Experimental and computational radial equivalence ratio traverses downstream from the nozzle mixing plane.
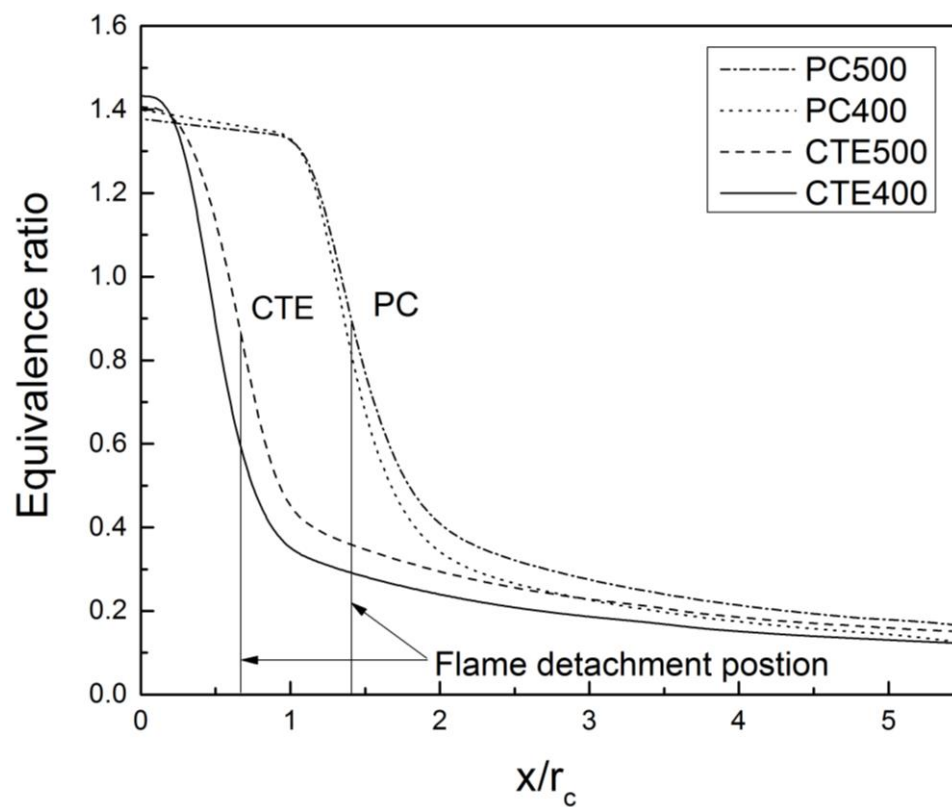

Figure 3. Computed equivalence ratio variations, along the centerline, for the two nozzles.

Temperature dependence of laminar burning velocities of low calorific value gases

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Abstract

Low calorific value gases become more and more important in several applications, due to energy efficiency and emissions aspects in industrial applications. The specific information and physic-chemical properties of these fuels are limited these days and classical knowledge of combustion of small-hydrocarbons cannot be transferred directly to these fuels. The laminar burning velocity is a fundamental property of reactive fuel-oxidizer mixtures, varying with composition, pressure and initial temperature and is very important for validation of reaction mechanisms and the specific design of burners for industry and household applications. Furthermore, within the "power-to-gas" concept, some new technologies arise to use renewable energy to produce hydrogen and utilize it as fuel. These fuel blends are of major interest since the hydrogen concentration in the gas grid system could increase of up to 25 vol. %. On the other hand, the change of the gas composition also changes the combustion properties, for example burning velocity, Wobbe-Index and ignition delay. There are several experimental methods to measure laminar burning velocity, e.g. the Bunsen flame method, the spherically expanding flame method, the stagnation flame method and the flat flame burner method, which also includes the heat-flux burner method. The accuracy of the different methods could be enhanced over the last years but there are still errors of up to 30 vol. % depending on method, boundary condition and fuel composition. Furthermore, for a lot of fuels, especially fuel blends, there is a lack of data.

In this study, the heat-flux burner method was applied to measure laminar burning velocities of low calorific value fuels, especially hydrogen containing fuel blends, for different temperatures. Therefore the different fuels are tested within a range of equivalence ratios from 0.5 to 1.5 for initial temperatures of 298 K up to 373 K at atmospheric conditions.
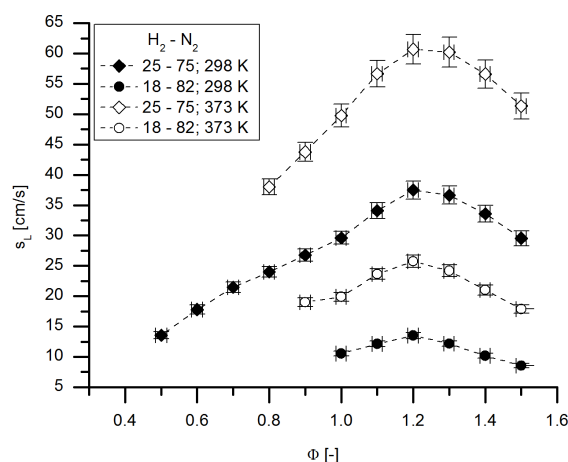
Figure 1 – *Laminar burning velocity of different H_2-N_2-air flames at 298 K and 373 K.*

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Spectroscopically Based Diagnostics in Laminar Flames with Overtone Transitions of $X^2\Pi$ Diatomics

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Laminar flames are often utilized e.g. for benchmarking the performance of chemical kinetic models [1] or laboratory-scale testing of the techniques suitable for practical diagnostics in industrial combustion devices. Spectral features of fundamental and overtone vibrations under high-temperature conditions ($T > 1000$ K) as well as hot bands structures leading to numerous coincidences with the lines belonging to different molecular species are inherent for these systems.

First overtone transitions of the OH radical (in the ground electronic $X^2\Pi$ state) in the near-infrared region were reinvestigated in the given context following the findings from previous studies [2]. Population of OH radical produced by combustion of methane–air mixtures in the atmospheric pressure flat-flame burner [3] were probed via wavelength modulation spectroscopy (WMS) technique. Predictions of high-resolution spectra for the given purpose were obtained from the HITEMP database [4] and numerical simulations of the flame structure (temperature and species concentration profiles) in one-dimensional representation (Fig. 1).

Prediction based on spectroscopic parameters needs to be performed if there is lack of validated data on spectral line positions and their strengths for desired molecular species or selected spectral range (e.g. for fluoromethylidyne radical, which is abundant in flames inhibited by the fluorinated fire extinguishing agents).

Overtone transitions of the CF ($X^2\Pi$) radical produced from the mixture of heptafluoropropene (CF_3CHFCF_3) and argon in the positive-column discharge were investigated by the means of time-resolved FTIR emission spectroscopy [5] in order to assign their spectra and to estimate if WMS in laminar flames is further realizable also in the case of fluorinated species.

Predicted positions of the CF ($X^2\Pi$) $1{\rightarrow}0$ transitions were obtained employing the Pickett's DPFIT/ DPCAT software suite. Spectral line positions of the ground & vibrationally excited states were taken from the literature [6,7]. Following this procedure overtone transitions of the $X^2\Pi$ radicals can be efficiently assigned in the emission spectra of discharge plasma. Thus we are able to estimate in such way if WMS in laminar flames is further realizable also in the case of fluorinated species.

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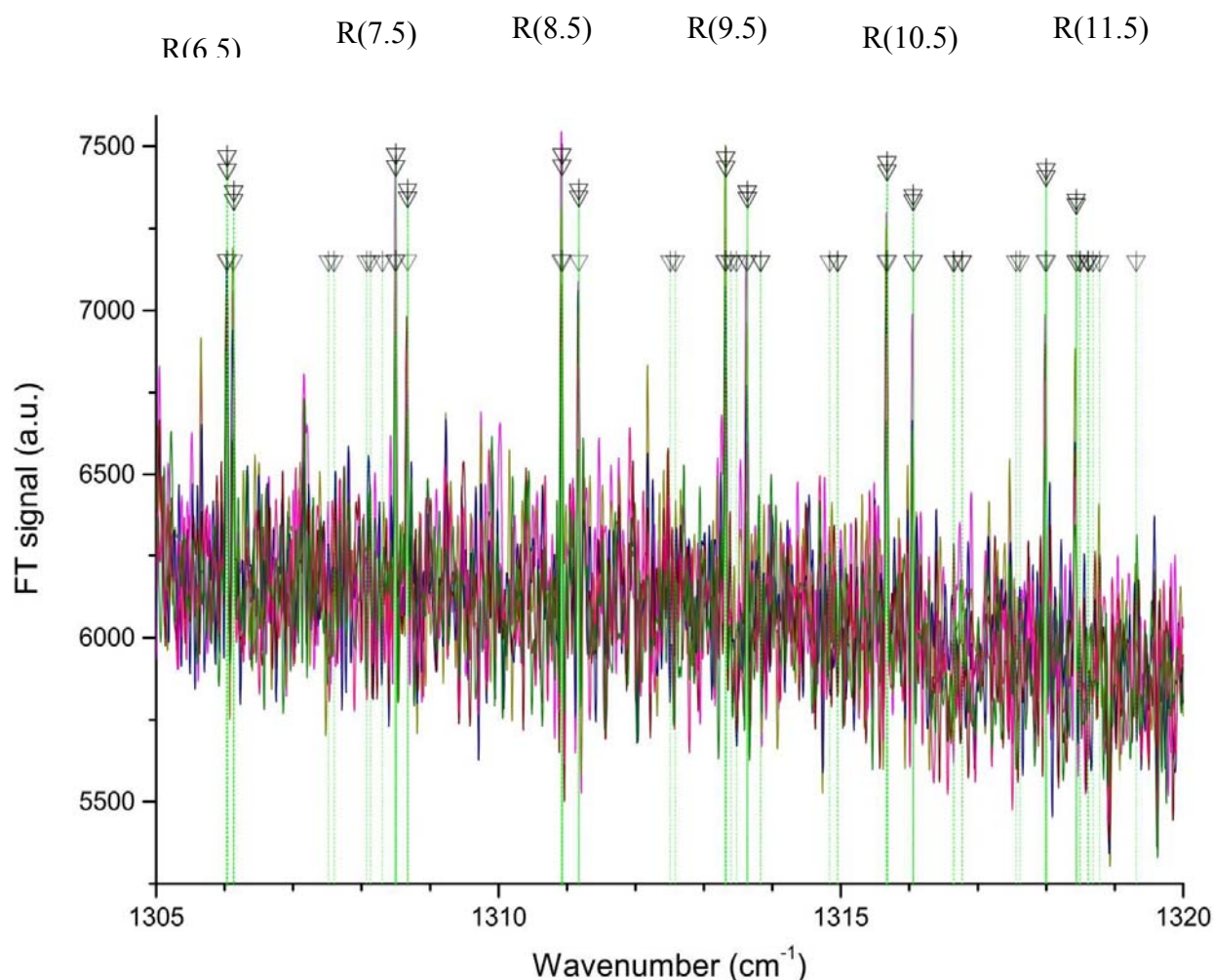
Fig. 1: Fundamental transitions of the CF ($X^2\Pi$) radical produced from the mixture of heptafluoropropene (CF_3CHFCF_3) and helium in the positive-column discharge were identified unambiguously by the means of time-resolved FTIR emission spectroscopy [5].

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Low-vacuum heating of tars relevant in combustion and material science

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Introduction

Tars, typically derived from coal and heavy fuel processing or formed in combustion, are complex mixtures of organic species with aromatic and aliphatic functionalities spanning from few hundreds up to thousands of Da of molecular weight (MW). Many different diagnostics are required for their characterization, nevertheless the identification of single molecular components is not straightforward, and the speciation of the huge number of aromatic molecules is only partially effective avoiding reaching the complete map of the tar composition.

In the present work a fractionation method based on low-vacuum heating has been preliminarily tested on synthetic mixtures of polycyclic aromatic hydrocarbons (PAH) presumed to be the basic aromatic moieties of tar components. The characterization of the separated components has been done to verify the operative conditions more favourable to an effective separation. The procedure has been also applied to a typical sample of combustion-formed tar and a synthetic pitch for tracing to their structure/composition.

Experimental

<u>Samples:</u> Three samples have been treated:
- PAH mixture constituted of: pyrene, coronene, benzo[b]crisene, pentacene, indeno[1,2,3 cd]pyrene.
-Flame-formed tar collected in a premixed laminar ethylene/oxygen flame (C/O=0.8), [1].
-Synthetic pitch obtained from naphthalene by catalytic reaction [2].

<u>Set-up and procedure:</u> A low-vacuum system [$P=10^{-6}$ mbar] was used for separating the lighter from the heavier fractions of tars. The samples were introduced in the crucible and kept for one hour at ambient temperature and a pressure of 10^{-6} mbar, after then the sample was kept at a temperature of 200°C for 1 hour.
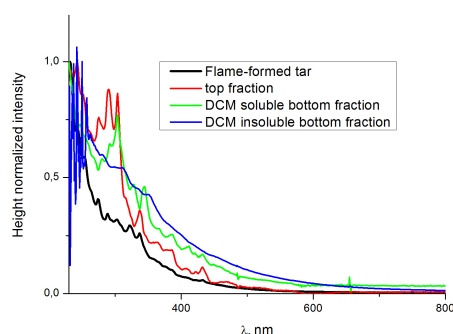
A quartz plate was placed at the top of the system both to visualize the evaporation process and as a suitable substrate for applying optical microscopy and spectroscopy to the condensed/deposited material. After the heating treatment, the material left in the crucible (bottom fraction) and that condensed on the quartz plate (top fraction) were recovered for the following characterization. In most cases, the bottom fraction could be fully recovered in dichloromethane (DCM), only in the case of partial solubilization, the insoluble material was recovered by N-methyl pyrrolidinone (NMP) dissolution. The solutions of the two fractions were further analysed by spectroscopic (UV-Visible absorption and fluorescence) and chromatographic (size exclusion chromatography, SEC) techniques.

Results and Discussion

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In the case of the PAH mixture, the heating at 200°C and P=10^{-6} mbar for one hour is sufficient for evaporating about 50 % of the starting mixture, as evaluated by weighting the fraction left in the crucible. The distribution of the PAH evaporated and deposited on the top was rather similar to the distribution in the starting mixture, as evaluated by deconvolution of the UV-Vis spectrum. The visual observation of the image under microscope of the quartz top revealed that the thickness of deposited film was not constant. In particular, although the film deposition is almost continuous along the entire surface, the presence of some grains where the material has coalesced was remarkable. It is noteworthy that the material on the top appears to be anisotropic by polarized light microscopy.

In the case of the flame-formed tar, the microscopic image of the material deposited on the top appears heterogeneous with the presence of both crystalline and liquid-like material. The microscopic observation put in evidence that the crystalline fraction is anisotropic whereas the liquid-like material is isotropic. The UV-Vis spectrum of the top material, dissolved in DCM, see figure, as well as the SEC analysis, confirmed the presence of heavier MW material with respect to PAH. It is known [1] that 30-40% of flame-formed tar is constituted of PAH, but a low-vacuum treatment, able to evaporate standard PAH, is not able to separate them from the heavier fractions present in tar.

The spectroscopic analysis of the DCM soluble and insoluble fractions of the bottom material, also reported in the figure, revealed the co-presence of PAH and high-MW aromatic species in the solubles and the almost total absence of PAH in the insolubles. It is conceivable that PAH interactions with the heavy matrix featuring the tar, are so strong to cause the dragging of some of the heavier fraction of tar during their evaporation. PAH and such heavy material could be just the species responsible for the crystalline and liquid-like morphology, respectively.

In the case of the synthetic naphthalene pitch, the microscopy image of the material evaporated and condensed on the quartz top revealed a uniform distribution of material that appeared completely isotropic at polarization microscopy.

It can be concluded that the effectiveness of the separation performed with this low-vacuum heating procedure depends on the complexity of the starting materials. However, the thin films obtained with this technique allow performing microscopy in order to obtain information on the self-organization of these condensed species.

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Insights of alkali metal ions role in steam assisted pyrolysis of xylan

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The presence of metals ions in biomass strongly affects pyrolysis product distribution promoting the formation of gaseous species and char at the expense of liquid fraction yield [1]. The role of inorganics on biomass components pyrolysis is far to be completely understood and deserves further experimental studies. The most abundant literature data are available only on the effect of metals ions on cellulose pyrolysis and hypotheses on decomposition mechanisms have been also formulated [2,3]. On the contrary only few works reported about the metal ions effect on the pyrolysis of the remaining biomass component, namely hemicellulose and lignin [4,5].

In the present paper the influence of metal ions on hemicellulose pyrolysis has been studied choosing commercial xylan (beechwood xylan, X4252 from Sigma Aldrich) as reference compound. Since commercial xylan presents a not negligible amount of metal ions (mostly alkali ions), a demineralization process was performed by using a cationic exchange resin. Results from ICP/MS analyses showed that an almost complete removal of the alkali metal ions (mainly Na) in the demineralized sample is obtained.

The thermal behavior of commercial and demineralized xylan samples has been studied in a thermogravimetric apparatus (Perkin-Elmer Pyris 1) at atmospheric pressure under an inert environment (N_2) from 50 °C up to 700 °C with a heating rate of 5 °C/min. Then steam assisted pyrolysis tests have been carried out in a proper experimental apparatus up to two different final temperatures, 600 and 700 °C, at pressure $P = 5 \times 10^5$ Pa and heating rate HR = 5 °C/min [6]. Products yields and gas releasing rate as function of the temperature, gas and liquid composition have been compared for raw and demineralized samples. The pyrolysis liquids, collected in a flask at the exit of the condenser, have been analyzed by liquid chromatography on an Agilent 1200 infinity high performance liquid chromatography (HPLC) instrument equipped with a quaternary pump, a UV/vis Diode Array and refractive index detectors. More experimental details are reported in [7].

The commercial xylan and demineralized xylan exhibited different thermogravimetric behaviors (Fig. 1, panel a). Commercial xylan decomposed over a temperature range between 200 °C and 320 °C, and two distinct events can be detected at 250 °C and at 300 °C. The final residue at 700 °C was 28.9 wt. %. Demineralized xylan decomposed over a slightly shorter temperature range (200 - 300 °C) with a main event peaked at 250 °C. The final residue at 700 °C was 23.8 wt. %. The presence of inorganic species as expected affects the char yield: commercial xylan produces a higher amount of char compared to the demineralized one. Of note, the presence of a second event into the thermogram of the commercial sample is probably due to a decomposition process promoted by inorganic species and thus absent in the demineralized sample.

Results obtained from pyrolysis tests at 600°C show that products yields are affected by the presence of inorganic species that depress the devolatilization of heavier compounds in favor of cracking reactions resulting in a lower yield of liquid. As shown in Fig.1 (panel b) the enhancement of cracking reactions in the untreated sample (X) results in a higher release of CO and CO_2 in the temperature range 250-400 °C. At higher temperature, the presence of inorganics depresses the release of CH_4 probably due to the lower extent of secondary reactions of the volatiles entrapped into the solid matrix.

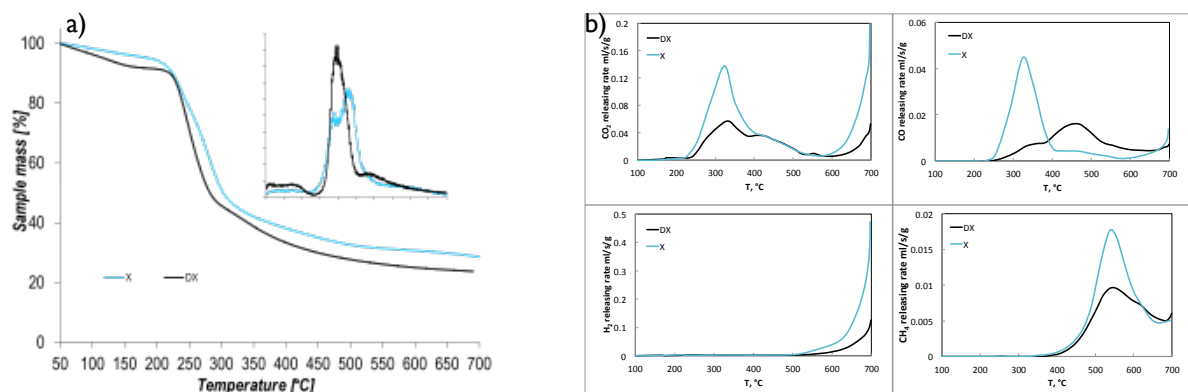*corresponding author*: Paola Giudicianni, giudicianni@irc.cnr.it

Figure 1. a) Thermogravimetric profiles. b) Releasing rate of the main gaseous species released from commercial (X) and demineralized (DX) xylan, as function of temperature.

Finally, at temperature higher than 600 °C, inorganics in the commercial xylan favor char gasification reactions resulting in a higher release of H_2 and CO_2.

The chromatographic analysis of pyrolysis liquids allowed the quantification of furanic derivatives (furfural, furfurylic alcohol, hydroxyl-methyl furfural (HMF), 5-methyl furfural) and the evaluation of the effects due to inorganic species (mainly alkali metals) also on pyrolysis liquid composition. The amount of furfural detected in the liquid fraction of the demineralized sample was around 18 $g/g_{feedstock}$ %, while the amount of HMF was an order of magnitude lower (0.16 $g/g_{feedstock}$ %) and that of furfurylic alcohol was even lower (0.07 $g/g_{feedstock}$ %). On the contrary, the presence of alkali metals in commercial xylan promoting the production of gaseous species depresses drastically the production of furanic derivatives (0.6, 0.15, 0.01 $g/g_{feedstock}$ % of furfural, furfurylic alcohol and HMF, respectively).

In conclusion this study showed that alkali metal ions affected both the devolatilization and gasification stages of xylan pyrolysis. More specifically, their presence depressed the furanic derivatives yield and enhanced the production of CO_2 and H_2 in the gasification stage. These preliminary results pave the way for enhancing the comprehension of hemicellulose pyrolysis and for the formulation of possible decomposition mechanisms.

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Reduction and optimization of reaction mechanisms for hydrogen and methane combustion with iron compounds

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Organic iron compounds are popular fuel additives and are known to affect strongly the combustion process [1]. Added to the fuel in order to modify the combustion kinetics or simply as a nanoparticle precursor. Usually, reaction kinetics of such additives is barely known but it is of essential interest if a) the metal compound has a strong impact on the flame kinetics and b) if the nanoparticle growth dynamic is of interest. In this context, iron compounds are well known to have a strong impact on flames, in particular ironpentacarbonyl was subject of investigation through past years [2,3].

The combustion process itself happens usually inside complex geometries or in a flame of complex geometry. It can be simulated only be means of computational fluid dynamics (CFD) in two- or three-dimensional space. Due to the strong impact of the additive on the flame structure, the reacting flow has to be described by a detailed mechanism and finite rate chemistry. On the other hand, the computational resources are limited and the number of species and reactions has to be reduced maintaining the reliability of the detailed description. In such cases the model reduction is limited to a skeletal mechanism, by a method which preserves the essential reaction paths (Fig. 1) or reaction steps.

In this work we present tools for reduction, optimization and manipulation of reaction mechanisms and their application in modeling the combustion of hydrogen and methane in presence of iron pentacarbonyl. The reduction and optimization methods are based on genetic algorithms [4,5]. The natural representation of the mechanism is binary coded for reduction and real coded for optimization, respectively. The methods are applied for premixed hydrogen/oxygen and for methane/oxygen flames doped with iron pentacarbonyl. The complexity of the algorithm is analyzed in comparison to a brute force method for mechanism reduction.The impact of uncertainty in rate constants and thermodynamic properties of intermediate reaction species is discussed, as well as the formation of iron clusters and particles which was neglected in older models [6].
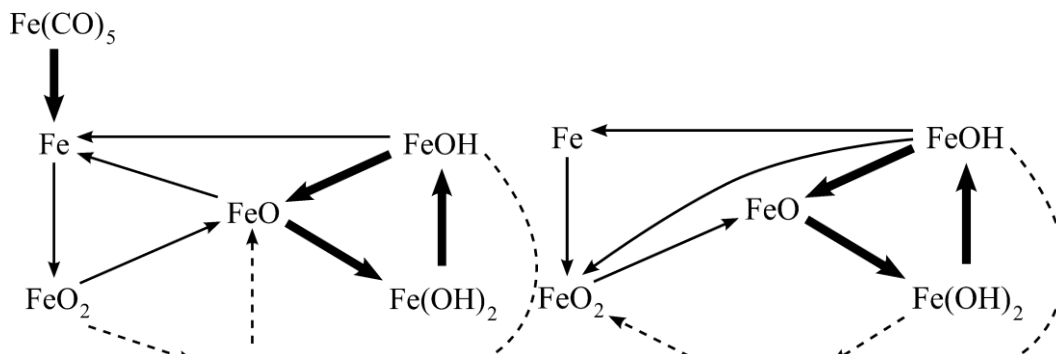
Figure 1 Reaction paths of the early flame (left) and the late flame (right). The dashed lines indicate reactions removed by the reduction procedure.

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Extension of the ReSpecTh database for application in a fully automated system for the development and validation of kinetic mechanisms

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Abstract

The increasing number of experimental data drive the extension, revision, and updating of complex kinetic mechanisms. The validation of such mechanisms requires the comparison of the results of kinetic simulations with a large number of experimental data, covering a wide range of temperature, pressure and dilution conditions.

On one side, the large number of data discourages extensive graphical comparisons of experimental datasets with the corresponding model predictions, and makes the definition of a quantitative and objective way to evaluate the mechanism mandatory [1]. The definition of a general, efficient and, most importantly, shared format to instruct a database for the storage of experimental data is one of the biggest challenges of the kinetic modelling community. If properly stored, such information can allow full automation of the validation process by linking the experimental database to standard kinetic solvers and postprocessors to iteratively and automatically assess the validity of the mechanism. Examples have been reported in the literature [2-6], but a general consensus is still far from being achieved.

This work presents the extension of the features of the ReSpecTh database developed in the Institute of Chemistry at Eötvös Loránd University (ELTE) [3] allowing the effective coupling upstream with the OpenSMOKE++ solver [7] and downstream with the Curve Matching framework [1].

Figure 1 shows the simplified entity-relationship diagram of the database implemented in this study. The database consists of the following main parts: 1) the "Experiment" section for storing the (x,y) data points. Once the experimental information is stored, the input files for the kinetic solver are automatically generated, explicitly declaring the desired output variables. The "Experiment" section contains many different tables useful for interpreting, reading, post processing and easily sharing the experimental data. For species measurements for example a table of species links the nomenclature used in the experimental studies with the names of the species in Chemkin format. To easily share the information, the storage structure in XML of the ReSpecTh database [3] has been adopted and to some extent modified to meet the needs of a fully automated system for the development and validation of chemical kinetic mechanisms. 2) The OpenSMOKE section containing all information needed for the kinetic simulation (type of reactor, inlet conditions, reactor conditions, observed variables) and 3) the Curve Matching framework to assess the validity of the mechanism.
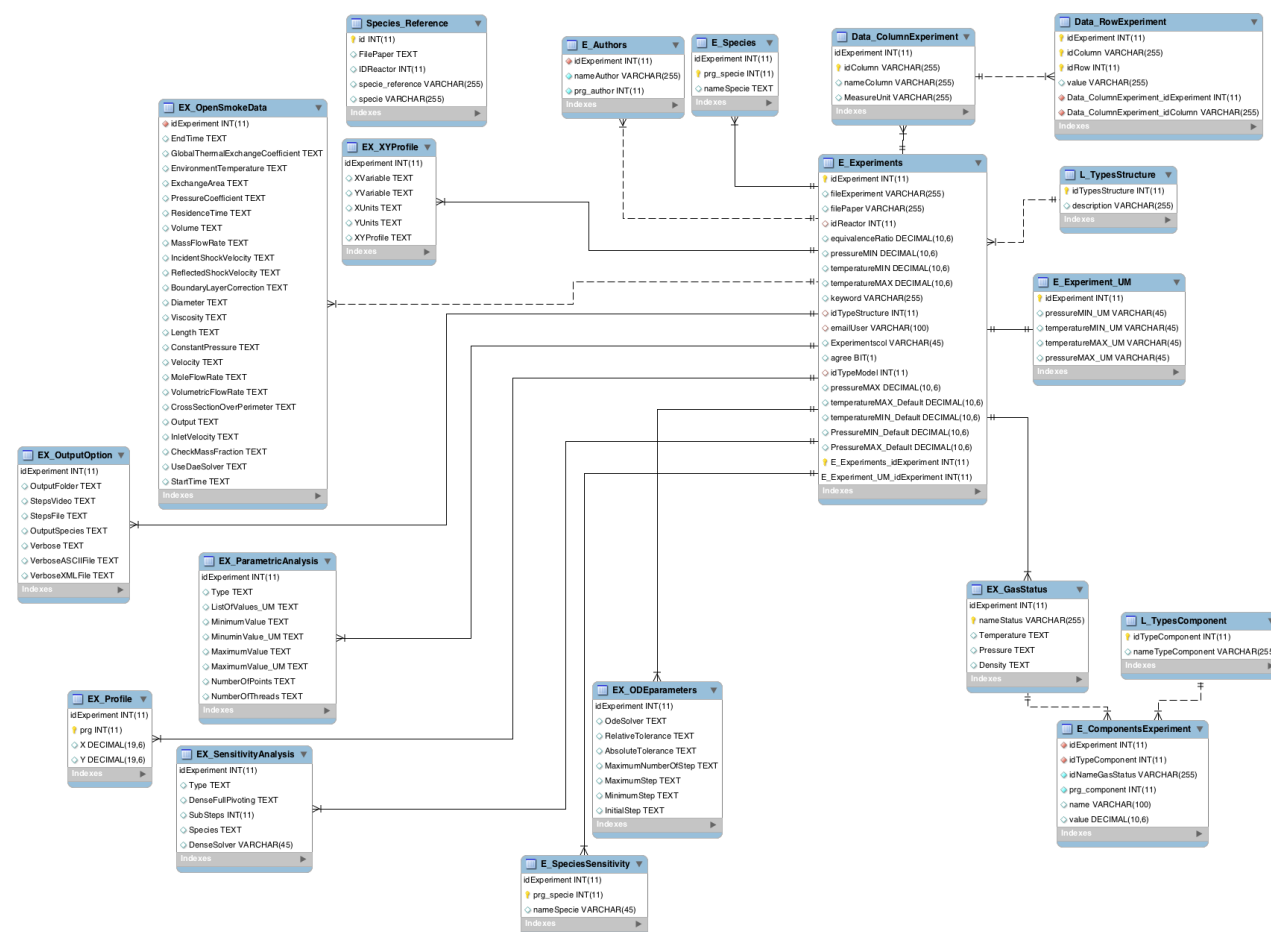
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Figure 1: Entity-relationship diagram of the database presented in this study.

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The impact of calcium and potassium on the pyrolysis and combustion of biomass

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The use of biomass for energy production has been increased over the last decades since it is considered as a renewable and CO_2-neutral energy source. However, there are still important issues, such as ash-related matters, that hinder its clean and efficient utilization in energy applications [1]. There is a wide range of sources for biomass production, and even for a specific biomass, different planting environments, harvest seasons, and different parts of the biomass can produce different ash contents and compositions [1].

Although the mineral content depends on the given biomass (see for instance [2]), calcium and potassium, respectively, are typically one of the main alkali and alkaline earth metals present in biomass. In this context, this work includes a systematic study of the influence of the presence and concentration of Ca and K on the pyrolysis and combustion of biomass, using grape pomace as the reference biomass.

To prepare the different samples, the raw grape pomace biomass was firstly demineralized by a nitric acid leaching procedure [3] and, subsequently, impregnated with different concentrations of either Ca (using calcium oxalate monohydrate as reactant) or K (using potassium oxalate monohydrate as reactant).

The different biomass samples were either pyrolyzed in N_2 atmosphere or oxidized in air in a thermo-gravimetric analyzer during non-isothermal runs at 10 K/min to a maximum temperature of 1275 K. The peak temperature where the burning rate, dX/dt (s^{-1}), is maximum is used to quantify the reactivity of the different samples and the temperature where the pyrolysis and oxidation curves separate each other to identify the ignition temperature (see Figure 1 as an example of the analysis procedure). In addition, these results have been used to determine the kinetics of the process.
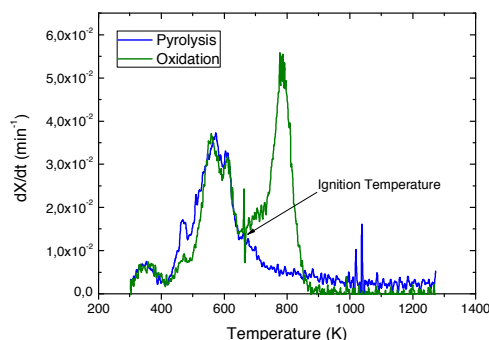

Figure 1 Pyrolysis and oxidation profiles of the demineralized biomass.

In particular, this work includes the analysis of the combustion behavior of raw grape pomace, demineralized biomass and biomass doped with 0.1% wt., 0.5% wt., 1.08% wt.

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(equal to Ca concentration in the raw biomass), 3% wt. and 6% wt. Ca and 0.1% wt., 0.5% wt., 0.82% wt. (equal to the K concentration in the raw biomass), 3% wt. and 6% wt. K. Figure 2 shows the rate of mass loss for all the samples considered in this work during their pyrolysis in a N_2 atmosphere.
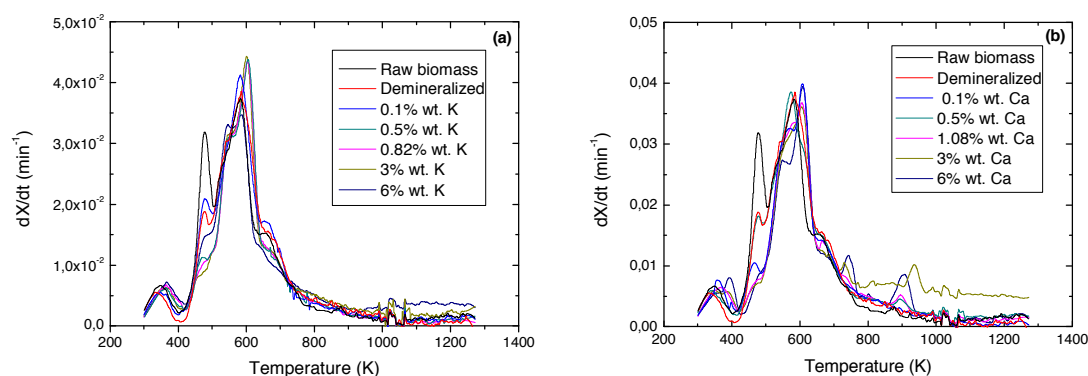

Figure 2 Pyrolysis profiles of raw grape pomace (Raw biomass), demineralized biomass and of the biomass doped with the different concentrations of K [a] and Ca [b].

After the first peak at 350 K that corresponds to the water release, the raw biomass shows three distinct peaks, which are generally associated with the release of the three biomass main components: hemicellulose, cellulose and lignin [4]. The curves corresponding to the demineralized biomass and the doped biomass show the three peaks at the same temperature as in the case of the raw biomass. However, the magnitude of the peaks is slightly affected by the biomass treatment. The magnitude of the first peak, associated with hemicellulose, is the most affected. It decreases when the biomass is demineralized and it decreases further when the biomass is doped either with K or Ca.

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Mathematical Modelling of Straw Combustion in a Moving Bed Combustor

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Abstract

Straw is renewable and environmentally friendly energy source that can be burned in direct combustion process to provide electricity and heat. Despite its apparent simplicity, direct combustion is a complex process from a technological point of view.

Conventional combustion equipment is not designed for burning agricultural residues. Devices for agricultural waste combustion are still in developing phase, which means that there is no good enough design solution on the world market yet. In order to construct a boiler and realise optimal combustion conditions, it is necessary to develop a mathematical model for biomass combustion.

In this study, an original numerical model for the surface combustion of straw in a moving bed is proposed and relevant equations solved using original programme realised in C++, to simulate heterogeneous characteristics of the burning process. Two-dimensional mathematical model includes: moisture evaporation, straw pyrolysis, gas product combustion and char combustion.

The model provides detailed information on burning processes in moving bed, which is otherwise very difficult to obtain by conventional experimental techniques. The model provides information concerning temperature front propagation, reaction front rate, as well as remaining gas species composition in bed.

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CFD Simulation of Co-combustion of Solid Recovered Fuel and Coal in a Cement Calciner

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Extended abstract – poster presentation

Disposal of large quantities of waste has a negative effect on human health, quality of life and particularly on the environment. Due to the named negative effects the European Landfill directive (1999/31/EC), prohibits the disposal of untreated waste in landfills. Consequently, a variety of waste-to-energy technologies are the focus of many research and development activities. One of these waste-to–energy technologies is the thermal utilization of Solid Recovered Fuels – SRF. SRF is defined as solid fuels prepared from non-hazardous waste materials intended for firing in industrial furnaces. The thermal utilization of SRF, especially the co-combustion of SRF with coal is increasingly gaining on importance in cement industry. One possibility for the control and investigation of the co-combustion process are CFD simulations. Early comprehensive information, parametric studies and initial conclusions that can be gained from CFD simulations are very important in handling modern combustion units. The purpose of this poster is to present a CFD simulation of the co-combustion process in a cement calciner. Numerical models of pulverized coal and SRF combustion were developed and implemented into the commercial CFD code AVL FIRE®, which was then used for the investigation. This code was used to simulate turbulent flow field, interaction of particles with the gas phase, temperature field, and concentrations of the gaseous species and the reaction products, by solving the set of conservation equations for mass, momentum and enthalpy that govern these processes. A three dimensional geometry of a real industrial cement calciner was used for the CFD simulation. The results gained by this simulation can be used for the optimization of cement calciner's operating conditions, and for the reducing of its pollutant emissions depending on coal-SRF ratio and composition of both fuels.

Figure 1 is the graphical representation of the results that can be obtained by a numerical simulation of a cement calciner. The figure shows from left to right, the limestone decomposition, CO_2 mass fraction, and produced lime particles inside the calculated cement calciner. The 'empty' limestone regions are where conversion of limestone to lime, to a large extent, has already been completed. It can be observed that the largest concentration of CO_2 is in the connecting cylinder where most of the calcination process, e.g. thermal decomposition of limestone, is taking place.

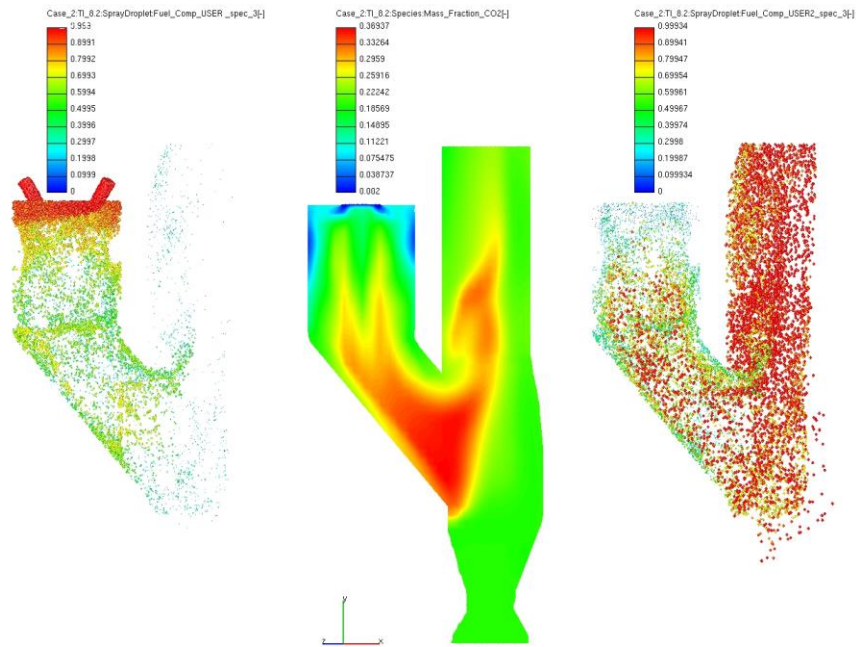*corresponding author*: Daniel Rolph Schneider, daniel.schneider@fsb.hr

Figure 1: Limestone decomposition (left); CO_2 Mass fraction (middle); Lime production (right)

Operating parameters adjustment of a diesel engine running with hydrotreated vegetable oil

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Introduction

European Union has established specific action plans for the promotion of biofuels in their markets. In 2007 the EU Commission put forth the ambitious "20/20" energy-climate package which included a 10% share of biofuels in the transportation sector by 2020. While the engine nominal settings are optimal for conventional diesel combustion, they are not anticipated to be optimal for biofuel combustion due primarily to its different physical and chemical properties. Hydrotreated vegetable oil (HVO) is a second generation biodiesel characterized by high heating value, high cetane number, no aromatic content, no oxygen content and low density compared to market diesel [1]. As a result, adjustments in operating parameters of the engine can potentially further improve the emission and combustion characteristics with HVO [2]. The impact of main injection timing (MIT), main injection pressure (MIP) as well as pilot injection timing (PIT) were examined in a common rail Euro 4 diesel engine of a small passenger car.

Methodology

A commercial market diesel as a reference fuel was compared with a 2nd generation HVO fuel in a Peugeot Euro 4 turbocharged diesel engine which is used in small passenger cars. The experiments were performed in thermally stabilized steady state operating points at two different engine speeds (1500rpm and 3000rpm). Three MIT strategies were investigated, a default MIT, 2° CA (crank angle) advanced MIT and 2° CA retarded MIT. Furthermore, variation of 300 bar increase of MIP was also examined. Finally, three PIT were investigated, where default PIT was advanced for 5°CAand retarded for 5° CA. During each case all the other operating parameters of the engine were kept constant with the EGR valve position at 0%. All experiments were performed at the Faculty of Mechanical Engineering , University of Ljubljana in Slovenia.

Results-Discussion

According to the findings, MIT settings strongly affect the combustion characteristics of a diesel engine and emission levels. The results have shown that advancing the injection timing by 2°CA produces higher in-cylinder pressure and increases oxidation process rate between carbon and oxygen molecules, thus results in reduction in THC and soot emissions, however, it significantly increases NO_x emission. On the other hand, during retarded MIT (by 2°CA), fuel injection starts later, as a result combustion duration decreases and therefore, incomplete combustion occurs. Retardation of MIT results in an increase of THC and soot emissions with marginal improvement in NOx emission. As HVO in general produces lower soot and THC emissions compared to market diesel,

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retardation by 2 crank angle degrees of MIT would be a good strategy to reduce all regulated emissions simultaneously.

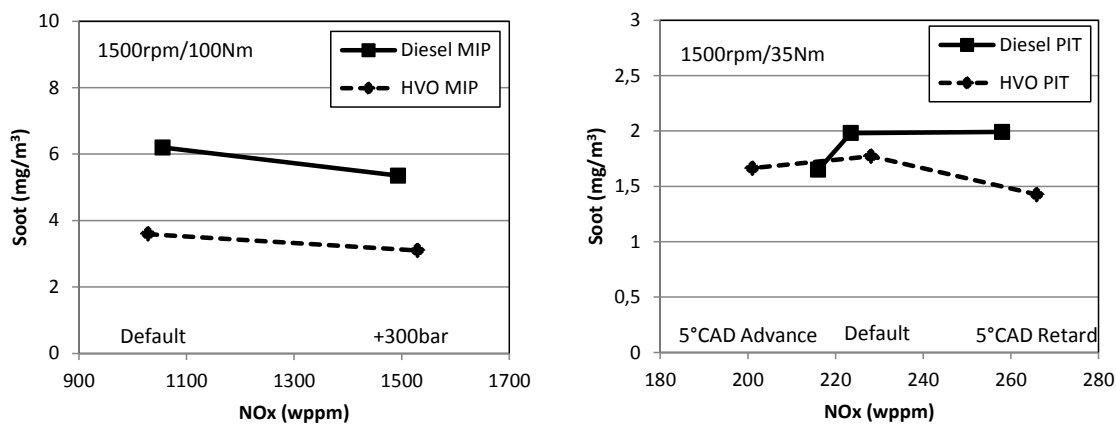| Properties	Unit	Diesel	HVO
FAME content	% v/v	7	0
Density at 60°C	Kg/m3	832.4	778.7
Sulfur content	Ppwt	9.1	<5.0
Cetane number	-	56.5	76.3
Water content	Mg/kg	160	20
Polyaromatic	%m/m	2.2	0
CFPP	°C	-5	-21
Heating value	MJ/kg	43	44
Distillation	°C	191-357	189-301
Oxygen content	% wt	0.77	0
H content	% wt	12	15.4
Carbon content	% wt	87.23	84.6

Figure 1 Effect of MIT, PIT and MIP on Trade off phenomena between soot and NOx emissions at 1500rpm

As far as the effect of MIP on emission levels is concerned, an increase by 300bar reduce further soot emissions with strong penalties to NO_x emissions in levels that exceed the levels of market diesel at default operating settings of the engine. The results have shown that increasing the main injection pressure with HVO fuel represents a good strategy only if the target is to reduce soot emissions.

Finally, the effect of PIT was also investigated. The results have shown that, when the PIT is advanced by 5° CA with HVO fuel, NO_x and soot emissions are reduced. As a result, in the case of HVO fuel, advancing the pilot injection timing is a very promising strategy to reduce NO_x and soot emissions simultaneously. In general by adjusting the injection parameters of a diesel engine with HVO fuel, advantageous fuel combustion characteristics as well as emissions could be achieved due to its different physical and chemical properties.

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Evaluation of different turbulent combustion approaches for modeling MILD Combustion in a cyclonic burner

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Abstract

Reducing pollutant emissions, increasing the fuel flexibility and improving burners efficiency has brought to the development of new combustion concepts. Among these new technologies, MILD combustion [1, 2] seems to be one of the most promising.

This is a combustion regime characterized by fuel oxidation in an environment with relatively low oxygen concentrations and high inlet temperatures. Such operating conditions feature a process with a distributed reaction zone, relatively uniform temperatures within the combustion chamber, no visible flame, low noise, negligible soot formation and very low NOx and CO emissions [3, 4].

Although MILD combustion systems have been successfully introduced in some industries, broad implementation is hampered by a lack of fundamental insight into this combustion regime.

Moreover, MILD combustion burners and furnaces often show a complex geometry designed to improve the reactant dilution through internal recirculation of flue gases, so that the derivation of simple conceptual models is difficult.

In this context CFD simulations for the prediction of the burner behaviour and for design and optimization appears essential for a successful introduction of such concept in some industries [5]. Detailed chemistry has to be included in fluid-dynamics simulations in order to account for the strong turbulence-chemistry interaction in the MILD regime.

Attractive strategies for including detailed chemistry effects using moderate CPU resources are tabulated chemistry techniques. Among such models are flamelet generated manifold (FGM) [6] techniques, which are based on flamelet assumption [7]. They have been applied to MILD combustion successfully [8].

On the other hand the Eddy Dissipation Concept Model, developed by B. Magnussen et al. [9], has the advantage of incorporating the influence of finite rate kinetics at quite moderate computational cost, which is quite moderate. The EDC model has been widely applied to MILD combustion systems, including JHC burners, and performs reasonably well compared to other standard combustion models [10].

Numerical simulations performed by Christo & Dally [11] using the EDC (Eddy Dissipation Concept) model showed reasonable agreement both quantitatively and qualitatively with the experimental results for oxygen concentrations of 9 % and 6 %.

In this framework the the primary goal of the present work is to assess the performance of both FGM approach along with finite rate kinetics based (EDC) combustion models and bring further insight to understand their accuracy and applicability to model the flames in MILD combustion regime

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The elucidation of the above topics needs high fidelity and comprehensive experimental data to validate the numerical models.

The numerical predictions obtained using the abovementioned models are compared with respective experimental data obtained in a cyclonic lab-scale burner that operates with high level of internal recirculation degrees and therefore emulates MILD conditions [12, 13]. Experimental tests were realized varying the mixture pre-heating temperatures and the mixture composition. Detailed measurements of local mean temperatures and concentrations of gas species at the stack for several operating conditions were used to validate the FGM model under such unconventional operating conditions. Results suggest that both the FGM and EDC models are promising tools for modeling the complex flame structures of cyclonic MILD burner, with many aspects that need to be further investigated.

In particular the profiles of the temperature and the mole fraction of major species (CH_4, H_2, O_2, CO, CO_2) obtained using FGM approach are in better agreement with the measurements compared to those obtained using EDC model; although, both the solution approaches fail to capture CO and H_2 profiles.

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Insights on complex carbonaceous material structure by mass spectrometric tools

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Introduction

In the present work, a method involving Fast Fourier Transform (FFT) analysis and a home-made software was applied for interpreting the mass spectra of complex PAH-laden samples derived from combustion systems and from heavy fossil fuels, thereby giving information on their composition. FFT analysis allows individuating periodicities that can indicate preferential growth routes and/or fragmentation patterns related to the chemical composition [1].The home-made software is able to sort large polycyclic aromatic hydrocarbons (LPAHs), which were found to be the major components in the complex mixtures, by their carbon number and double bond equivalence (DBE) number. Iso-abundance plots were introduced to sort and visualize the molecular constituents into different types based on the carbon and double bond equivalence (DBE) numbers [2].

Experimental

Samples: Soot was collected in premixed laminar flames of ethylene. The organic species adsorbed on soot were extracted with dichloromethane (DCM) and analyzed by mass spectrometric tools. More details on the experimental conditions and procedures are given elsewhere [3]. The petroleum pitch and the CARBORES coal tar pitch here named PP and CTP, respectively were kindly provided by RÜTGERS Basic Aromatics GmbH:.

Laser desorption ionisation time of flight mass spectrometry (LDI-TOFMS)
Positive Linear LDI-TOFMS spectra were recorded on a 4800 Plus MALDI TOF/TOF Analyzer (Applied Biosystems).

Mass spectrometric tools: The graphic software (Origin) has been used for calculating Fast Fourier Transform (FFT) [1].
A home-made software was used to assign the molecular formula to the main peaks detected in the mass spectra, by considering that the atomic weight of one H atom is 1.0086 Da and the accurate atomic weight of one C atom is 12.000 Da. Based on the assigned elemental compositions, the carbon number and double bond equivalence (DBE) number were determined for each mass peak and iso-abundance graphs were drawn in the Origin software by plotting the DBE number and the relative intensity against the carbon number. DBE number is defined following [4], as: $DBE = C-(H/2)+1$.

Results and Discussion

The LDI-TOFMS spectra of soot extract, CTP and PP extended from m/z 200 to 2000.
For soot extract, the two sequences of peaks with gap at m/z 12 and 24 up were remarkable In a previous work [5] such sequences up to about m/z 1000 have been attributed to even- and odd-numbered PAH. In the case of CTP, the FFT shows the predominant presence of gaps at m/z 12 and 24 along with a gap at m/z 14. The m/z gap 14 (CH2) suggests the presence of a series of LPAHs with the same aromatic core size but increasing number of short (methyl and ethyl) alkyl groups, such as. For the PP, the

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spectrum appears more complex and crowded of peaks, hindering an easy extrapolation of repetitive spacing without mathematical tools. The FFT analysis revealed only the presence of m/z gap of 14.

For each molecular formula the carbon number and the DBE were transformed into one dot and reported in iso-abundance plots with the color of the dot representing its relative content. The percentage of each species is calculated on the mass peak intensity ratio to the sum intensity of all mass peaks in the spectrum.

The iso-abundance plots of the three samples, reported in the Figure, show interesting features: first, the PP shows the variable and high intensity region in the 30-50 nC range.
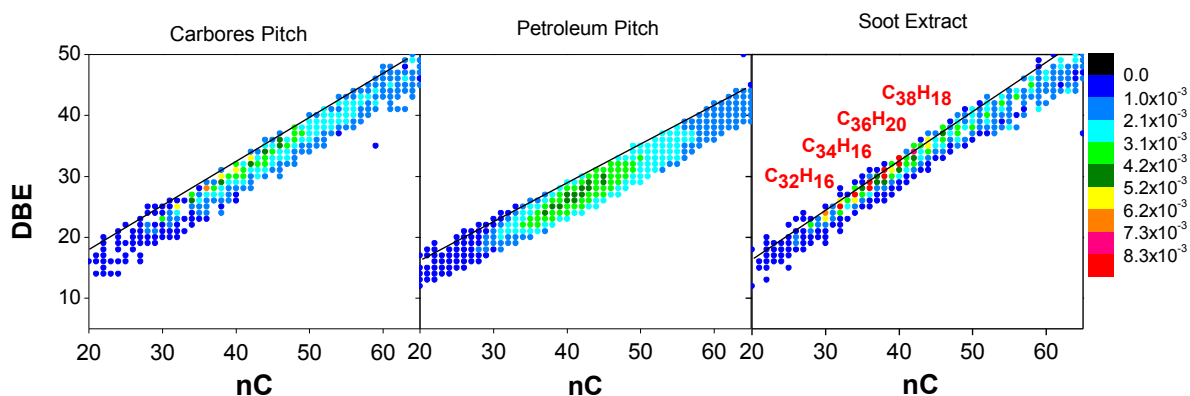
By contrast, CTP shows a slightly changing peak intensity along all the range. For soot extract, the exception is represented by the presence of some peaks with the higher intensity (red point on the right graph in figure) which correspond to the even PAH sequence of the well-known stabilomers grid in the range m/z 400-522 [6]. Moreover, iso-abundance plot distribution of CTP and soot extract is narrower demonstrating that the variety of LPAH species is smaller with respect to PP. For quantifying the differences among the three samples, it was used a planar limit line, introduced by Kim et al. [7]. The planar limit lines are generated by connecting the maximum DBE at given carbon numbers and are thus also relevant to the growth of the most fused molecules during carbonization. The slope of planar limit lines, namely DBE/carbon number ratios, for the linear and nonlinear integration of benzene rings to the precursor aromatic unit is 0.75 and 1, respectively. The slope obtained for the CTP is 0.7133, which indicates that LPAHs in the CTP are mainly formed by the linear and nonlinear extension with benzene rings. The slope for the PP is 0.6434. This indicates that, besides the growth of the aromatic core by integration of aromatic rings, the formation of saturated cyclic rings or the addition of saturated alkyl chains is also a possible reaction. Soot extract presents a slope of 0.8101, much higher with respect to the two pitches, indicating a higher aromatic nature of the sample. It confirms that the flame-formed organic species are mainly constituted of LPAHs with highly condensed aromatic cores with either no or short aliphatic side chains.

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