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Analysis, uncertainty quantification, validation, optimization and reduction of detailed combustion mechanism for practical use of Smart Energy Carriers

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A safe, secure and environmentally friendly energy supply is among the highest priorities and concerns of contemporary society. Currently, combustion of conventional and alternative fuels accounts for about 80% of total gross energy production in Europe. The greatest challenge that the combustion community has to face in the coming years is the urgent need for maximum fuel flexibility of combustion technologies, the minimization of greenhouse gas (GHG) emissions and the adjustment of distributed energy production. Fuel flexibility is a prerequisite to exploit a fast changing fuel market and an increasing number of energy carriers available. Mitigation of GHG emissions is a central priority of the EU Framework Programme for Research and Innovation Horizon 2020 and it is clear that a multifaceted approach, encompassing highly efficient low-carbon technologies coupled with medium-term emission containment (e.g. Carbon Capture and Storage/Utilization), will have to be pursued in order to avoid potentially catastrophic climatic consequences. The realization of a new energy production and distribution system based on smart grid concepts is often seen as a possible straightforward option for developed countries.

The COST Action Chemistry of Smart Energy Carriers and Technologies (SMARTCATs- CM1404, www.smartcats.eu) has the primary aim of creating a Europewide network of world leading academic and research institutions and key industries to promote the use of Smart Energy Carriers (SECs) on a large scale in order to increase fuel flexibility and carbon efficiency of energy production and to support distributed energy generation strategies.

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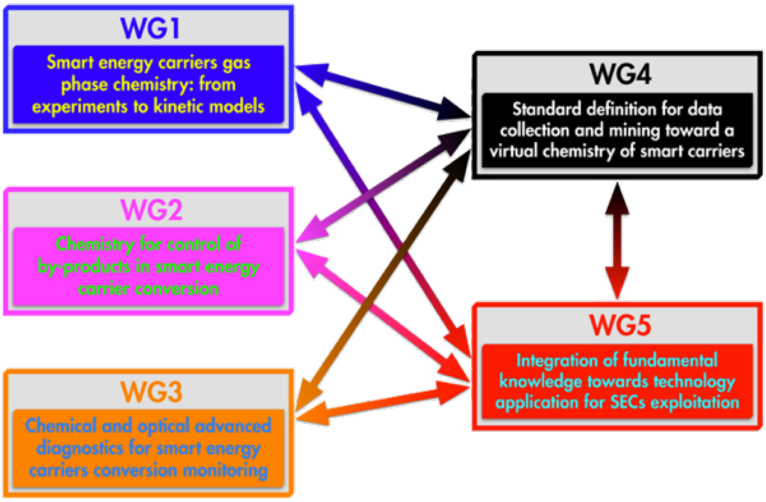

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Scientific Scope of the training school

Combustion phenomena can be interpreted by detailed kinetic reaction mechanisms consisting of several hundreds or even thousands of reaction steps. It may be important to determine the key reaction steps that drive the overall reactivity of the chemical system or the production of key species. It may also be necessary to include the chemical mechanism within a larger model describing, for example, a reactive flow problem. In this case the smallest version of the mechanism describing key kinetic features may be required in order to meet the limitations of the computational requirements. Mechanism reduction techniques can identify the core reactions in a large mechanism and the application of reduced mechanisms may speed up the simulations, allowing engineering optimizations. It may also be important to determine the predictability of any model which incorporates the chemical mechanism, and therefore to assess the confidence that can be placed in simulation results. Uncertainty analysis allows the calculation of the uncertainty of simulation results based on the users' best knowledge of the input parameters, potentially putting an error bar on model predictions. Sensitivity analysis can provide the subsequent identification of the most important parameters driving model uncertainty. These methods can form a key part of the process of model evaluation and improvement.

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Optimization of detailed combustion mechanisms for C1/C2 oxygenate fuels

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Development and validation of a detailed chemical kinetic mechanism for prediction of NO_x-SO_x synergies.

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The environmental interest in 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). In this context, a detailed chemical kinetic mechanism has been developed in order to study the effect of NO and SO_2 on the oxidation of CO-H_2 mixture and CH_4 in a jet stirred reactor at atmospheric pressure and for various equivalence ratios (i.e. ϕ: 0.1, 1.0, 2.0 for the CO-H_2 mixture and ϕ: 0.1, 0.5 for the CH_4) and initial concentrations of NO and SO_2 0-5000 ppm as per the CO-H_2 mixture and 0-1000 ppm as per the CH_4. The simulations were performed at fixed residence time (i.e. 120 msec for the CO-H_2 mixture and 120, 240 msec for CH_4) and variable temperature within the range of 800-1600 K. Computational results are validated against experimental speciation data ([1] [2]). Results yield a solid basis for comprehensive understanding of the effects and synergies between NO_x and SO_x on hydrocarbon oxidation. 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 marine engine simulations.

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Uncertainty Quantification of chemical kinetics for non-conventional combustion regimes

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For its ability to couple high efficiency with very low pollutant emissions, Moderate or Intense Low-oxygen Dilution (MILD) combustion is becoming more and more popular. MILD conditions can be reached by heating up and diluting the fuel stream with the hot flue gases. Because of the strong interactions between chemistry and fluid dynamics, there is a need for a detailed mechanims while simulating these conditions. Available detailed mechanisms have been proven to be inadequate for these conditions. The focus of this research is to enhance the preformance of available detailed chemical mechanisms for non-conventional combustion regimes, through the use of uncertainty quantification and minimization. The initial test case considered is a PFR, based on simulations and experiments from [1]. In this case the ignition delay time of methane dilluted with N_2 at different inlet temperatures and C/O ratios were evaluated. The simulations in this work were performed with the software OpenSMOKE++ [2, 3] and the uncertainty quantification was performed with the so called Bound-To-Bound Data Collaboration (B2B-DC) [4] method. As an initial step the parameters of the reaction, which showed highest sensitivity to temperature at the moment of ignition, was evaluated. The results show that by changing only the Arrhenius constant and the activation energy gives you local consitency for each C/O ratio at an error bound of 20%. To reach global consitency, the number of parameters needs to be increased. Also other parameters such as third-body efficiencies and chemical effects of the dilutant should be considered.

This project has received funding from the European Unions Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No 643134.

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Low-temperature oxidation of diethyl ether containing mixtures: development of a mechanism and kinetic modelling

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Diethyl ether (DEE) can be used as diesel additive and as ignition improver for ethanol [1-3]. Furthermore, the safety engineering is interested in predicting the ignition behavior of DEE because it is a common used solvent. Moreover, DEE can be used to investigate safety-relevant ignition processes on hot surfaces [4].

For a better prediction of the ignition behavior of DEE we develop a low-temperature oxidation mechanism. The mechanism is divided into a DEE-specific part and a base mechanism from Burke et al. [5, 6]. This base mechanism contains the reactions of C_1-C_4 species and of the H_2/O_2-system. The DEE-specific part was formulated analogous to the oxidation mechanism of dimethyl ether [7] and contains the characteristic low-temperature oxidation pathways of alkanes: H-atom abstraction reactions, O_2-addition to the DEE radical, isomerization, a second O_2-addition and the chain branching reactions of ketohydroperoxide decomposition. The Arrhenius parameters and thermodynamic data were estimated by structure-reactivity relations. The modeled ignition delay times were compared to ignition delay times measured in a rapid compression machine (RCM) and a shock tube [8]. For low pressures there is a good agreement between the chemical kinetic model and the RCM measurements whereas for high pressures further adjustments to experimental data are needed.

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Reduction of Ammonia/Methane & Ammonia/Hydrogen Combustion Mechanisms for the Modelling of Zero Carbon Power Production

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The development of renewable and environmentally benign alternatives to fossil fuels is a critical challenge facing our society. One such alternative being explored is the utilization of ammonia as a clean energy carrier that can be produced from renewable sources. Ammonia, a hydrogen rich fuel, has the potential for carbon free combustion, exhausting only water and nitrogen. The well-established infrastructure in industry for the production, transportation and storage of ammonia, further adds to its viability as a fossil fuel replacement. Yet, significant barriers to ammonia combustion still need to be addressed prior to its practical implementation as a fuel, namely:

- A high resistance to auto ignition.
- The production of NO_X due to the fuel bound nitrogen.

The blending of ammonia with combustion enhancers, such as methane[1] and hydrogen[2], has been explored in literature, as a possible solution to the first issue. But, in order to elicit the chemical and mechanical combustion parameters needed to limit the production of NO_X, a detailed chemical understanding of the combustion mechanism for these ammonia-methane/hydrogen blended fuels is required. To this end, several detailed reaction models of ammonia combustion (considering 85-128 species and 779-1200 reactions) have been proposed[3–5]. However, the utilization of such detailed mechanisms in practical simulations to address the aforementioned issues, is computationally expensive. Thus, a reduced mechanism, with the ability to capture the main chemical and thermochemical details of the reaction, is needed to expedite the process.

In this work the combustion model of ammonia/methane and ammonia/hydrogen blends developed by Konnov[5] is examined. The formation and consumption fluxes of each species at multiple reaction path generations are analysed to identify the important reaction pathways and the associated species. Using the Path Flux Analysis method of Sun et al.[6] and Gou et al.[7] as implemented in the Chem-RC software[8], a number of reduced kinetic models are developed, ranging in species and reaction size. The accuracy of these models is then numerically and experimentally evaluated in the example scenario of replacing methane in a Spark Ignition engine.

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Experimental and kinetic modeling study of the pyrolysis of cyclopentadiene: realistic pathways from C_5H_5 to naphthalene

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A combined experimental and theoretical study is presented, aiming at understanding the formation of polycyclic aromatic hydrocarbons. A single-event kinetic model for the pyrolysis of cyclopentadiene (CPD) was created using the automated reaction network generator, RMG, and complemented with ab initio calculations to accurately predict the formation of indene and naphthalene. In agreement with literature [1], indene is found to be produced primarily from C_5H_5 + CPD, following a complicated series of isomerizations. The process leading to naphthalene ($C_{10}H_8$) starts with recombination of two cyclopentadienyl radicals. The single-step reaction $C_5H_5 + C_5H_5 \rightarrow C_{10}H_8 + H + H$ suggested in literature [2] does not suffice to model the formation of naphthalene. Instead, the dominant path leading to naphthalene is multi-step [3], and involves a third radical reactant. In the present study the numerous isomerization reactions that take place on the $C_{10}H_{10}$ and $C_{10}H_9$ surfaces are accounted for. The newly developed kinetic model is consistent with product yields measured during the pyrolysis of pure cyclopentadiene [4] and those measured during the co-pyrolysis of cyclopentadiene and ethene, performed as part of this work.

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Computational fluid dynamics simulation of the diesel injector internal and external flow for different nozzles

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The Diesel spray quality emerging from the injector nozzle of multi-hole injectors is highly affected by the internal geometry of the injector. The characteristics of diesel spray jet quality, namely jet breakup length and spray ligaments and droplets dispersion, as well as the resulting spray shape are considered as very important parameters for the creation of an optimized spray and for the preparation of the combustible air/fuel mixture. The main objective of the present work was to model the full three-dimensional Diesel injector geometry and examine the nozzle entry geometry effects on the expected cavitation phenomena in the nozzle and on the pattern of the emerging liquid jet. The three-dimensional geometry of a valve-covered orifice sac-less six-hole Diesel injector was investigated for four geometries which included two short length nozzles and two long length nozzles, with a sharp entry and a rounded entry, each. The computational domain of the symmetrical one sixth of the injector was assembled with a constant volume chamber, and the Eulerian modelling methodology with the volume of fluid method and the Rayleigh cavitation model were used for simulations for fully open needle. It was found that cavitation phenomena occur in the nozzles when the entry is sharp, while cavitation phenomena are limited for nozzles with rounded entry. It was observed that when cavitation is present there is asymmetry in the velocity profiles at the nozzle exit the air-fuel mixing and turbulence are more pronounced at the upper area of the jet where cavitation preceded in the nozzle. Comparison of the simulation against published experimental images of the cavitation pattern showed that there is good qualitative agreement.

The Influence of n-Butanol Blending on the Ignition Delay Times of Gasoline and its Surrogate at High Pressures

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The influence of blending n-butanol at 20% by volume on the ignition delay times for a reference gasoline was studied in a rapid compression machine (RCM) at 20 bar from 678 K- 858 K. Delay times for the blend lay between those of stoichiometric gasoline and stoichiometric n-butanol across the temperature range studied. At lower temperatures, delays for the blend were however, much closer to those of n-butanol than gasoline despite n-butanol being only 20% of the mixture. Under these conditions n-butanol acts as an octane enhancer over and above what might be expected from a simple linear blending law. The ability of a gasoline surrogate, based on a toluene reference fuel (TRF), to capture the main trends of the gasoline/ n-butanol blending behavior was also tested within the RCM. The 3-component TRF based on a mixture of toluene, n-heptane and iso-octane was able to capture the trends well across the temperature range studied. Simulations of ignition delay times were also performed using a detailed blended n-butanol/TRF mechanism based on the adiabatic core assumption and volume histories from the experimental data. Overall, the model captured the main features of the blending behavior, although at the lowest temperatures, predicted ignition delays for stoichiometric n-butanol were longer than those observed. A brute force local sensitivity analysis was performed to evaluate the main chemical processes driving the ignition behaviour of the TRF, n-butanol and blended fuels. The reactions of fuel + OH dominated the sensitivities at lower temperatures, with H abstraction from n-butanol from the alpha and gamma sites being key for both the n-butanol and the blend. At higher temperatures the reactions of HO2 and that of formaldehyde with OH became critical, in common with the ignition behaviour of other fuels. Remaining uncertainties in the rates of these key reactions are discussed.

First Principles Based Microkinetic Modelling of Methyl Butanoate Pyrolysis

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The increasing worldwide energy demand and reduced amount of petroleum reserves have created the need for sustainable development of alternatives. One of the possible alternatives is biodiesel, a fuel substitute produced from renewable resources such as vegetable oils or animal fats. An understanding of the reactivity of the oxygenated part of these molecules is still required. Methyl butanoate (MB), CH3CH2CH2C(=O)OCH3, is a relatively short methyl ester that still incorporates all essential chemical structure features of a typical biofuel. It can therefore be used as a convenient model compound for the complex biofuel methyl ester mixture.

In this work, an ab initio based group additive model is built to describe the pyrolysis of methyl esters. The kinetic model is validated by comparison with a new set of experimental data gathered on a flow reactor. For the pyrolysis of MB, the feed to the reactor is set to 257 g/h MB and 40 g/h N_2. The pressure is set to 0.17 MPa. In order to cover the complete conversion range, the temperature setting varies from 913 K to 1113 K in 20 K increments.

For the development of the first principles based microkinetic model for MB pyrolysis, the Genesys [1] software package for automatic kinetic model generation is used and adapted. The termination of the kinetic model generation is achieved with the rule-based criterion. For the determination of thermodynamics and kinetics of all compounds and reactions in the model, Genesys makes use of user-defined databases. These databases contain thermodynamic and kinetic data for hydrocarbon and oxygenated compounds that are calculated with CBS-QB3 composite method. If data is not available for certain compounds or reactions, estimation techniques are used. For thermodynamic data this includes Benson's group additivity method [2] and hydrogen increment method [3]. For rate coefficients, the group additivity method[4, 5] is used or analogy with reactions taken from literature data[6, 7].

The simulated MB conversion and major product yields agree well with experimental data acquired at the experimental setup over the studied temperature range. The majority of the major products are simulated within less than 10% relative deviation from the experimental values.

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Turbulent Combustion and Auto-ignition of Alternative Engine Fuels

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The current trend of downsizing and turbo-charging engines to reduce fuel consumption increases the possibility of engine knock and therefore requires fuels which are more resistant to auto-ignition [1]. Auto-ignition can be defined as the onset of self-sustained combustion of the mixture in the absence of an external source of ignition, such as a spark or flame. The addition of bio-fuels such as bio-ethanol and bio-butanol to conventional gasoline can reduce greenhouse gas emissions and probably offer a better knock resistance than traditional fossil fuels, thereby improving engine performance. However, it is debatable which biofuel offer the most benefits in terms of overall potential.

This research will investigate the effects of such alcohol fuel blends with gasoline and Toluene Reference Fuel (TRF) mixtures on ignition delay times and excitation times. Ignition delay times are in the range of milliseconds and will be obtained through experimental work on a Rapid Compression Machine (RCM). However, excitation times, during which the heat release occurs, are of the order of microseconds and can only be obtained through numerical simulations.

The study will determine the reactions that are significant in determining the two times. They are incorporated in the theoretical detonation peninsula and provide a more fundamental approach to prevention of engine knock than use of Octane Numbers.

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NO$_x$ reduction in grate-fired waste-to-energy plants
Budapest, 4-7 July, 2016

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Managing the large amounts of municipal solid waste that is produced daily is a significant challenge, and R&D efforts to resolve the problems are increasing. Traditionally, municipal solid waste has been disposed of at landfills due to the low cost. In many regions this is no longer possible as an increase in municipal solid waste generation is experienced. Furthermore, according to the European Landfill Directive, the use of landfills has to be avoided whenever possible [1]. This has generated a shift in municipal solid waste handling, from disposal at landfills to extraction of energy through combustion. One of the main combustion technologies for solid waste is grate-firing [2]. This technology is widely regarded as one of the most competitive, as it enables the use of a wide range of fuels, both biomass and solid waste, with varying moisture content, and the need for fuel preparation and handling is limited [3].

Combustion of solid waste, similar to combustion of other solid fuels, emits nitrogen oxides (NO$_x$). The emission of NO$_x$ continues to be a major environmental concern [4] as it is an acid rain precursor and participates in formation of photochemical smog, which is problematic in urban areas [4,5].

The combustion in a waste-to-energy (W-t-E) plant is split into two regions: a fuel rich region where limited oxygen is available, and a fuel lean region which acts to secure full conversion of the combustible gasses from the fuel lean region and full conversion of the char. The combustion technique (staged combustion) is developed to secure low NO$_x$ formation as NO$_x$ acts as an oxidizing agent when oxygen is not present. Optimal distribution between the primary combustion air, provided under the grate, and secondary and tertiary combustion air was evaluated through PFR simulation using a Detailed Chemical Kinetic Model [6] and a developed model for determination of the devolatilisation gas composition from devolatilisation of municipal solid waste during combustion. The simulations showed that a minimal NO$_x$ level can be achieved by controlling the oxygen to fuel ratio (λ) in the fuel rich zone. Furthermore, by decreasing the temperature in this zone a further reduction in NO$_x$ can be achieved.

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Chemical kinetic modelling of combustion-generated nanoparticles
Budapest, 4-7 July, 2016

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Combustion generated nanoparticles include both organic (soot, carbon black, etc.) and inorganic (silica, silicon, titania, etc.) materials. Chemical kinetics modelling for silicon nanoparticles synthesis [1, 2] and soot formation [3] is presented. Computational Modelling Cambridge Ltd. (CMCL Innovations)'s proprietary software kinetics™ is used to model the two use cases. Reactors parameterization (hot–wall and IC engine) and mechanism reduction are also carried out using kinetics™. CMCL's MoDS (Model Development Suite) is used for model calibration and to perform sensitivity and uncertainty analysis on the model parameters. Kinetic mechanism reduction using DRG and DRG-EP strategies is implemented to the gas-phase pyrolysis of the silicon precursor silane and to the soot formation mechanisms. Particulate phase modelling of soot formation is also presented and includes a detailed high-dimensional population balance sub-model solved using the method of moments.

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Dual fuel combustion process – investigation of kinetically controlled processes in diesel substitution engines

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The dual fuel combustion process combines the compression ignition of a diesel engine with the premixed lean combustion of a gas engine. The combustion processes are complex and are not yet fully understood. On the one hand the spray conditioning and ignition of the diesel fuel has to be considered, on the other side lean premixed combustion of the gas engine has to be taken into account.

To be able to investigate the ignition process, flame speed and the formation of pollutants, the development of a detailed reaction mechanism for diesel/natural gas mixtures is aspired. For simulation, appropriate surrogates for diesel and natural gas will be used. Based on already available reaction mechanisms for these surrogates, a combined detailed reaction mechanism will be developed. In a further step this reaction mechanism will be used for CFD simulations. Therefore, to reduce the calculation effort, the reaction mechanism has to be reduced, where the detailed reaction mechanism will be used as reference.

Toward a complete model including soot formation from the dimethyl carbonate pyrolysis.

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Dimethyl carbonate (DMC, $CH_3OCOOCH_3$) is an attractive oxygenate compound for using as diesel fuel component for reducing soot emissions due to its good characteristics, such as: (1) 100% miscibility in diesel, (2) 53 wt% in oxygen content, (3) no carbon–carbon atomic bonds, and (4) relatively high H/C ratio. In this way, this work aims to investigate the sooting tendency of DMC under pyrolytic conditions in a flow reactor at atmospheric pressure, in a wide range of temperature (1075-1475 K) and with different inlet DMC concentrations (33333 ppm and 50000 ppm). Experimental facility was described elsewhere (e.g. [1]). The experimental data were compared with the results of a detailed gas-phase chemical kinetic model. The chemical reaction mechanism was built based on Alzueta et al. [2] mechanism. Reactions involving benzene, toluene, and other intermediates such as phenyl radicals were added to this base mechanism. The mechanism was also extended to include different pathways for the polycyclic aromatic hydrocarbon (PAH) formation, specifically: (1) H-abstraction/C_2H_2-addition (HACA) (starting with the C_2H_2 addition to phenyl radical), (2) the combination of phenyl radicals with benzene, (3) the cyclopentadienyl radicals recombination, and (4) the combination of benzyl and propargyl radicals. The rate constants proposed by Appel et al. [3] for PAH growth up to pyrene and the rate constants for the PAH growth from pyrene up to coronene proposed by Richter et al. [4] were used. Mechanism for the PAH oxidation by Appel et al. [3] was also added. In this way, the kinetic model only includes gas-phase chemistry and does not include soot particle dynamics.

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Experimental Study of Ammonia Ignition

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Ammonia has been considered as a potential clean alternative energy carrier for automobile engines and gas turbines because of its production from renewable sources using concepts such as power-to-gas. It is regarded to be a carbon free fuel and burns in an environmentally benign way, producing no soot. However, knowledge of NOx and other pollutant formation in engines at high compression ratios is lacking. A detailed understanding of combustion characteristics of ammonia over a wide range of conditions is required for fuel-engine optimization and for its use in conventional and advanced engines.

The present study focusses on ignition delay time measurements of ammonia/air mixtures in a high pressure shock tube and in a rapid compression machine facility. Experiments were carried out over the temperature range of 1000 - 1500 K, pressures of 20 and 40 atm, and equivalence ratios of 0.5, 1.0 and 2.0. The experimental results are used for detailed kinetic model development and validation.

Ions as sensitive indicator for neutral polycyclic aromatic hydrocarbons in combustion processes

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Combustion is the basis of 80 % of the world-wide energy conversion and will not lose its importance in the coming decades. On the one hand, this type of energy conversion ensures a certain level of economic wealth, while on the other hand, it harms our health and accelerates climate change by its emissions such as polycyclic aromatic hydrocarbons (PAH). Consequently, improvement of combustion devices with respect to their efficiency and emissions control is of particular importance. Chemical kinetic reaction mechanisms that describe the oxidation of fuel and pollutant formation give further insights into the pathways of the decomposition of the fuel. Time-of-flight mass spectrometric in-situ measurements of model- flames are used to get a fundamental understanding of combustion [1]. To describe the flame chemistry sufficiently, neutral molecules have to be identified. During the sampling process, condensing material can block the nozzle and reduce the sampling efficiency [2]. Consequently, in combustion analysis PAH in a certain mass range are hard to detect. Due to their role in soot formation as soot precursors and the health hazards they pose in combustion emissions, their formation mechanisms in fuel-rich flames are of great interest [3]. Sampling charged species from flames improves sampling efficiency for PAH and allows measurement of species, which often elude detection in molecular-beam-sampling systems. The derived mass spectra contain PAH in a small to intermediate size range and give an insight into PAH growth and soot precursor formation in flames [4]. Major questions concerning place of formation of the ions and their ability as indicator for neutral species should be answered in this work. Calculated equilibrium temperature profiles for the predominant reactions give an insight into the place of formation, which differs between the formation in a flame or in the molecular beam. When the place of formation is totally understood ions can be used as sensitive indicator for neutral species in flames. Data sets including equilibrium temperature profiles of predominant reactions and concentration profiles of the major species and key soot precursors have been obtained in methane flames for future reaction mechanism development and validation.

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Reduction and optimization of reaction mechanism for gas phase synthesis of nanoparticles

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Nanoparticles are an unwanted byproduct of combustion or are generated from flames on purpose. Of high importance are metal oxide nanoparticles which emerge from flames doped with metalorganic compounds. 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 iron pentacarbonyl was object of investigation through past years [1-3].

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 flame chemistry has to be described by a detailed mechanism. On the other hand, the computational resources are finite and the number of species and reactions has to be reduced maintaining the reliability if the detailed description. The reduction is limited to a skeletal mechanism.

In this work we present tools for reduction, optimization and manipulation of reaction mechanisms. The reduction and optimization steps 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 low complexity of the algorithm is analyzed in comparison to a brute force method.

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A global reduced mechanism for strained oxy-methane diffusion flames

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A global reduced mechanism is derived for strained laminar counterflow methane diffusion flame simulations under oxyfuel conditions with GRI 3.0 as the starting chemical mechanism. Using Directed Relation Graph (DRG), DRG-aided sensitivity analysis (DRGASA) and unimportant reaction elimination methods, unimportant species and reactions are identified and subsequently removed from the starting mechanism. The final skeletal mechanism is further shortened by using the steady state approximation. The resulting reduced mechanism, which is benchmarked against the starting detailed mechanism, reproduces with a good accuracy the flame temperature profile, profiles of major and intermediate species, the maximum flame temperature profile and the value of the strain rate at extinction.

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Combustion chemistry of Smart Energy Carriers in model reactors

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The use of advanced combustion technologies, such as MILD combustion [1], is among the most promising methods to reduce emission of pollutants, as the system working temperatures are enough low to boost the formation of several classes of pollutants. To access this temperature range, a significant dilution as well as preheating of reactants is required. These features also imply a strong fuel flexibility, thus allowing the use of low calorific values mixtures with high efficiency. The high content of diluent species, deriving either from the presence of diluent in low calorific values fuels or from the recirculation of flue gases to reach MILD combustion regime, namely CO_2 and H_2O makes the role of these species relevant in the oxidation chemistry in such a non standard condition [2].

The aim of the present work is to highlight the effect of CO_2 and H_2O on the ignition and oxidation kinetics in two model reactors. More specifically, ignition delay times have been experimentally evaluated in a Plug Flow Reactor using propane and a model gas surrogating the gaseous fraction of biomass pyrolysis products containing C1-C2 species, CO and CO_2. The experimental analysis has been carried out at atmospheric pressure, in a wide range of inlet temperatures and equivalence ratios, for mixtures highly diluted in N_2, or CO_2, or H_2O.

Experimental tests have also been carried out for propane/oxygen/nitrogen mixtures in presence of variable amount of CO_2 and in a Jet Stirred Flow Reactor. The experiments have been realized at atmospheric pressure, over the temperature range 800-1150 K, from fuel lean to rich conditions and at a residence time of 0.5 s.

Temperature and species concentration measurements obtained in the Jet Stirred Flow Reactor, along with the ignition delay times obtained in the Plug Flow Reactor, suggest that the ignition and oxidation processes of simple fuels are significantly altered by CO_2 and H_2O in dependence of mixture inlet temperatures and equivalence ratios.

Numerical simulations for studying the ignition and oxidation processes in the same working conditions of experimental tests have been carried out by means of several kinetic models available in the literature. It has been shown that kinetic models are not able to correctly reproduce the experimental results. In particular CO_2 and H_2O alter the main radical branching mechanisms, i.e. in termolecular reactions as third body species with high collisional efficiencies or directly participating in bimolecular reactions.

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3D multi-physics modeling approach to study the behaviors of monoliths and foams catalysts for the lean methane combustion

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Although NG is one of the cleanest hydrocarbon fuels, the complete oxidation of CH_4 from compressed NG-fuelled (CNG-fuelled) engines is still an open issue. Catalysts for CH4 combustion undergo very demanding conditions: they must resist thermal and mechanical shocks and exhibit high activity, as CH_4 molecules show great stability and the temperature of the exhausts in CNG vehicles is relatively low (> 500 °C) [1]. Typical sources of CH_4 emissions include leaks in gas transportation facilities such as pipelines and compressor stations, upstream oil and gas production facilities, and coal beds [2]. For the latter source, CH_4 represents a hazard when the coal is mined in an underground mine and must be removed to ensure workers safety. Many catalysts have been used for the combustion of CH_4, with Pt and Pd being the most common active metals, although also perovskites or perovskites with noble metals have been employed. Recently attention has increasingly focused on the development of cobalt oxide based powders. These powders have high potential for use as catalysts, gas sensors, magnetic materials, rechargeable batteries, pigments for ceramics solar energy adsorbers and electrochemical devices [3],

Ceramic and metallic monoliths are widely used as catalyst supports in environmental applications for automotive exhausts and reduction of nitrogen oxides. Innovative area for monolith based catalysts is gas-solid endo/exothermic processes which require multi-tubular packed bed reactors [4,5]. An amount of 0.2 g catalysts was deposited on monoliths by Solution Combustion synthesis and impregnated with Pd by Incipient Wetnees Impregnation. The activity of synthesized catalysts towards CH4 combustion in lean conditions was measured was measured by means of temperature programmed oxidation (TPO). A gas mixture of 2%, 1% or 0.5% CH4 in N2, with an excess of oxygen ($\lambda=4$) at a 30, 60, and 90 WHSV was used during the tests. CH4, CO, CO2 and O2 outlet concentrations were monitored by a ABB analyzer equipped with a thermal conductivity detector.

The aim of the work is to use the experimental data to validate a model to investigate some kinetics phenomena impossible to detect experimentally. For this aim a 3D multi-physics, multi-phase, multi-component and not iso-thermal model was developed to analyze the effects of catalyst structures on the combustion reactions. The model includes Stokes-Brinckman, Maxwell-Stefan, and Flory-Huggins equations solved by Comsol® Multiphysics v4.4 platform.

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Particulate matter and gaseous emissions from small scale pellet stove for different fuel quality R&D Activities at the University of Belgrade, Faculty of Mechanical Engineering

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Biomass pellets (especially wood pellets) is one of the most used forms of produced solid biomass fuel for generating heat energy in Serbian households last few years. This type of solid biofuel allow more efficient combustion process in stoves and boilers as well as higher automatisation. For testing purposes of small scale pellet combustion appliances for household heating in order to meet actual demands for efficiency and emission limits, experimental installation is developed and constructed according to SRPS EN 14785. This paper presents some of the results of experimental testing of small scale pellet stove (up to 10 kW) with three different test fuels – wood pellets at nominal heat output. Presented results are obtained from two independent tests for each test fuel. Combustion, energy and environmental characteristics (CO and particulate matter emissions) and their dependence of the fuel quality were analysed. In addition, regression analysis was performed on test results and correlations for considered characteristics were established, as well as quality parameters of regression analysis.

Thermochemical conversions of biomass and WB lignites R&D Activities at the University of Belgrade, Faculty of Mechanical Engineering

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The Faculty of Mechanical Engineering as part of the Belgrade University (UB-FME), among others, has departments and chairs dealing with different energy and environmental topics: Fuel and Combustion, Process and Environmental Engineering, Thermomechanics, Motor Vehicles and Internal Combustion (IC) Engines. UB-FME partners with industry and government agencies to create more efficient, less polluting and more flexible energy solutions. The Fuel and Combustion Laboratory (FCL) and Department for process and environmental engineering (DPEE), creates value and innovation through knowledge generation and development of technological solutions that are brought into practical use. In this regard, here are presented some of research activities at The FCL and DPEE. In the same time, UB-FME is participated in different FP7 and Horizon 2020 projects.

Since pyrolysis is the first step of thermochemical conversion such as gasification, liquefaction, carbonization, and combustion, its sound understanding is significant for the effective use of fuels (coal and/or biomass). A satisfactory understanding of pyrolysis process can give rise to a dramatic development of thermochemical conversion process. For engineering applications, knowledge of the pyrolysis kinetics is essential for predicting the pyrolysis behavior of biomass and fossil materials as well as designing the suitable reactor. Therefore, experimental and modeling results of lignite and corn cob pyrolyisis are presented. The pyrolysis behavior of two pulverized lignites from Eastern Europe was investigated particularly in respect to the kinetics of pyrolysis. Two rapid heating methods, the heated wire mesh and a Pyroprobe have been used to determine the yield of the volatiles. The kinetic parameters for pyrolysis have been obtained by thermogravimetric apparatus and by wire mesh experiments. The experimental data were compared with theoretical values predicted using the theoretical model coal pyrolysis, model FG-DVC and with other studies on lignites. Two different corncob samples from different continents and climates were studied by thermogravimetry at linear and nonlinear heating programs in inert gas flow. A distributed activation energy model (DAEM) with three and four pools of reactants (pseudocomponents) was used due to the complexity of the biomass samples of agricultural origin. The resulting models described well the experimental data.

Combined kinetic and quantum chemical analysis of an organocatalytic reaction between propanal and nitrostyrene

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Organocatalysis has gained remarkable attention in the past decade due to the clear advantages of their applications in stereoselective chemical transformations. These reactions are promoted by small, metal-free organic compounds, which are typically moisture and air tolerant, and they (or their building blocks) are readily available in nature. Among the variety of organocatalytic transformations, enantioselective Michael additions between aldehydes and nitroalkenes catalyzed by diarylprolinol derivatives have been the subject of intensive mechanistic studies highlighting the desire for comprehensive understanding. Recent investigations have pointed to the importance of experimentally observed cyclic reaction intermediates [1-3], however, views on the specific role of these species is still controversial.

With the aim of gaining further insight, we analyzed kinetic profiles that follow the concentration of experimentally observed species. Trial models were built based on the previously proposed mechanism taking several different possibilities under consideration for the cyclic intermediate consuming reaction steps. Comparison of these models suggested that the reaction pathway proposed by us [3] (involving the protonation of the oxazine oxide intermediate) is significantly faster than the formerly suggested alternative [2]. Moreover we could give a new mechanistic explanation [4] for the reaction between the cyclic intermediates and the water content of the mixture which was supported by kinetic simulations and DFT calculations.

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Asymptotic Analysis of a Target Mediated Drug Disposition Model: Algorithmic and Traditional Approaches

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A detailed analysis is reported of a multiscale pharmacokinetic model, simulating the interaction of a drug with its target, the binding of the compounds and the outcome of their interaction. The analysis is based on the algorithmic Computational Singular Perturbation (CSP) methodology. Among others, the analysis concludes that the partial equilibrium and the quasi steady state approximations (QSSA and PEA) are valid in two distinct stages in the evolution of the process. Similar conclusions are reached from the algorithmic criteria for the validity of the QSSA and PEA. The reactions in the pharmacokinetic model that (i) generate the fast time scales, (ii) generate the constraints in which the system evolves and (iii) drive the system at various phases are identified, with the use of algorithmic CSP tools. These identifications are very important for the improvement of the model and for the identification of ways to control the evolution of the process. Regarding the qualitative understanding of the process , the present analysis systematises the findings in the literature and provides some new insights.

Creating a reduced mechanism for simulating combustion of small alcohols

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Fossil fuels are generally agreed to cause environmental damage, and because of that alternative fuels, such as small alcohols [1], are becoming more used across the world. Simulating combustion reactions can be an important step in the development process of future vehicle engines, power generation burners, or any other internal combustion engine. Using a detailed mechanism that contains all possible reactions, and all intermediate species, is computationally feasible for smaller fuels in simplified combustion systems. However, simulations of real combustion devices such as engines are computationally very expensive and the detailed chemistry is too time consuming to resolve. The more complex the fuel is, the more reactions there are, and thus the simulation time is further increased.

The time problem can be solved by using reduced mechanism. Reduced mechanisms are models used to simulate combustion processes, but contains fewer reactions and intermediate species. A benefit of detailed mechanisms is that they represent the true chemistry, and only contain real molecules and reactions, and thus the results are trustworthy. A reduced mechanism on the other hand, does not have to contain real molecules, nor does it contain every possible reaction, but is limited to the most prominent. To validate the results of reduced mechanisms, the reactions are tuned, using some optimization method, until it matches the results of a detailed mechanism. A method of tweaking reaction coefficients is called simulated annealing [2], which is a probabilistic method of finding values for the coefficients in order to minimize the deviation between results of the reduced and the detailed mechanism.

There are several ways of developing reduced mechanisms. One possible way is to use principal component analysis [3]. This method starts from a detailed mechanism and looks at how sensitive the results are to changes in rate parameters for each reaction. Then, reactions (or intermediate species) that do not affect the results much are removed. If this is done correctly, it is possible to acquire a model that simulates reality almost as well as a detailed mechanism, but is much faster, and can thus be used in more complex systems.

The goal of the present project is to develop reduced mechanisms for small alcohol fuels. The mechanisms should be small enough to be useful in Large Eddy Simulations (LES) and accurate enough to predict fundamental combustion properties like ignition, propagation and extinction of flames. Another goal is that the mechanisms should be able to predict concentrations of major product species CO_2 and H_2O, but also specific minor products of particular importance to alcohol combustion, like acetaldehyde and formaldehyde.

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Detailed Kinetic Mechanisms for Combustion and Oxidation of Natural Gas

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Recently, considerable attention has been paid to natural gas, because it burns more cleanly than other hydrocarbon. The aim of this study is to propose a detailed kinetic mechanism for combustion and oxidation of natural gas. The kinetic characterization of natural gas combustion represents an important and crucial role to correctly predict and describe the flame characteristics and stability. Even though, the accuracy of combustion schemes have been improved in recent years, nonetheless, no specific scheme with well predictability for unconventional combustions (oxy-fuel and flameless) has been introduced. With this goal, this work explores a detailed kinetic mechanism with predictive capabilities in a wide range of operating conditions (conventional and unconventional) oxidation and combustion of natural gas. Therefore, Modelling of methane combustion and oxidation in a wide range of operating conditions was carried out, but only highlighted result is shown here. The reported comparisons with the experimental data show a good agreement; however, there exists the possibility of further improvements.

The application of agricultural waste and recycling products small and medium scale boilers. Project AGROBIOATENA

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The objective of the project is to carry out research on physical and chemical properties of various types of ready-made biofuel, derived from agricultural waste and recycling products such as straw, its mixes, inedible grains, and on application of this fuel in small and medium scale boilers.

Over 25 different agricultural waste and recycling products were selected for the research, and our laboratory determined physical and chemical parameters, i.e., calorific value, ash content, major and minor elements, ash fusion characteristics.

In the course of the project, a layout of a heating device was developed; experimental and numerical investigations of fuel combustion in furnaces were performed seeking to optimize combustion process and to find ways to reduce ash fusion in the combustion chamber and concentrations of pollutants emitted during the combustion process.

In order to avoid ash fusion, a two-chamber combustion boiler was designed and manufactured; in the first chamber, the fuel is gasified with air deficiency and the temperature from 450° C to 550° C, and in the second chamber, with additional amount of air, it is completely combusted.

During the experiments thermal parameters and emissions in combustion products were continuously recorded to gather information for further development actions

Optimization of detailed combustion mechanisms for C1/C2 oxygenate fuels

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A detailed reaction mechanism was developed that can be used for combustion simulations of small oxygenate fuels such as methanol, ethanol, formaldehyde and acetaldehyde. Previous optimization studies of the authors focused exclusively on either C1 or C2 fuels. It was found that ethanol combustion mechanisms are often not able to capture important combustion phenomena related to methanol combustion, which motivated the authors to develop a universally applicable reaction scheme.

Starting from the ethanol combustion mechanism of Leplat et al. [1] and adopting the H2/CO base chemistry from the optimized hydrogen/syngas mechanism of Varga et al. [2] as well as the methanol chemistry of Li et al. [3], an optimization of 90 Arrhenius parameters of 28 important elementary reactions was carried out. The self-reaction of HO2 was revisited as more chemical information could be inferred from the available experimental data than in the previous study of Varga et al. [2]. The newly optimized Arrhenius parameters for this reaction provide more realistic and accurate rate coefficients at both, high and low temperatures.

Optimization targets included a wide range of experimental data such as ignition delays, laminar burning velocities and species concentration profiles and direct rate coefficient measurements, as well as theoretical rate determinations. In total, 29449 indirect measurement points in 443 datasets were used, together with 124 direct measurement series and 65 theoretical rate determinations. The data collection was stored in the ReSpecTh Kinetics Database XML format and will be made accessible to the combustion community. The present work presents the most comprehensive application of the optimization method of Turányi et al. [4] to date.

The final optimized mechanism was compared successfully to several published C1/C2 reaction mechanisms with respect to the accuracy in reproducing the available data. In addition to providing best fitted values for the Arrhenius parameters, the covariance matrix of the optimized parameters was calculated, which describes the temperature-dependent uncertainty ranges for the optimized rate coefficients.

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