Fuels, Processes, and Combustion Physics in the Energy Transformation

715. WE-Heraeus-Seminar

08 – 12 March 2020
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 715. WE-Heraeus-Seminar:

The 2015 Paris United Nations Climate Change Conference postulates a limitation of global warming of less than 2°C as a minimum goal to revent a substantial change of the earth's climate. To reach this goal, the emission of greenhouse gas emissions has to be drastically reduced. Politically independent studies show that for industrial nations such as Germany, the necessary 95% reduction of greenhouse gas emissions by the year 2050 can only be realized by a radical transformation towards renewable concepts for electricity and heat supply, mobility, and industrial processes. This necessitates a rapid development of technologies to preserve natural resources, which will have to comprise a largely increased variety of different thermo-and electrochemical processes. A substantial part of thermo-chemical processes is based on combustion technologies, which need to be converted to using renewable fuels within only a few years. The necessary innovations require a high level of knowledge and understanding of the fundamental coupled physical and chemical processes. Furthermore, mathematically-based modeling techniques are needed to support predictive design of new processes by numerical simulations. In this context, the goal of the seminar is to identify the challenges associated with the transformation of energy and mobility systems, to discuss the state-of-the-art, and to highlight research needs. Besides invited presentations on mobility and the energy economy, also combustion technologies that go beyond the purpose of energy conversions, for instance for material synthesis, will be discussed. Further to the intense scientific exchange, also different viewpoints of industry, associations, and national research laboratories will be considered in the discussions.

Scientific Organizers:

Prof. Andreas Dreizler	Technische Universität Darmstadt, Germany E-mail: dreizler@rsm.tu-darmstadt.de
Prof. Heinz Pitsch	RWTH Aachen University, Germany E-mail: h.pitsch@itv.rwth-aachen.de

Program

Program

Sunday, 08 March 2020

16:00 – 20:00	Registration	
18:00 – 19:30	*BUFFET SUPPER and get-together*	

Session Chairs: A. Dreizler, H. Pitsch

19:30 – 20:00	Andreas Dreizler Heinz Pitsch	**Welcome and introduction**

Keynote lecture:

20:00 – 21:00	Katharina Kohse-Höinghaus	**Combustion perspectives: Some contributions from physical chemistry**

Monday, 09 March 2020

07:30	*BREAKFAST*	

Session Chair: U. Riedel

08:30 – 09:30	Viktor Scherer	**Waste derived fuels: significance, challenges, solutions**
09:30 – 10:30	Burak Atakan	**Piston engines for polygeneration**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:20	Francesco Contino	**Uncertainty quantification of energy systems**
11:20 – 11:40	Liming Cai	**Highly-automated model development for promising e-fuels from renewable electricity**
11:40 – 12:00	Paulo Debiagi	**A fundamental model of char oxidation**

Program

Monday, 09 March 2020

12:00	*LUNCH*	

Session Chair: Y. Wright

13:30 – 14:30	**Poster presentations**	
14:30 – 16:00	**Poster session** *and COFFEE*	
16:00 – 17:00	Olaf Deutschmann	**Controlling the emissions of internal combustion engines: Current status and future challenges**
17:00 – 18:00	Konstantinos Boulouchos	**Towards a better understanding of reactive thermofluidics in I.C. engines - potential and limitations of direct numerical simulation**
18:15	*HERAEUS DINNER* *(social event with cold & warm buffet with complimentary drinks)*	

Program

Tuesday, 10 March 2020

07:30	*BREAKFAST*	
Session Chair: A. Kempf		
08:30 – 09:30	Osvalda Senneca	**Thermal annealing of coal and biomass: from combustion science towards new carbon materials**
09:30 – 10:30	Benedicte Cuenot	**Large Eddy simulation of turbulent combustion in gas turbines**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:20	Arvind Gangoli Rao	**Energy transition in aviation: The role of cryogenic fuels**
11:20 – 11:40	Isaac Boxx	**An experimental study of hydrogen-enriched natural gas swirl flames in a gas turbine model combustor**
11:40 – 12:00	Bo Shu	**Experimental and modeling study on the auto-ignition properties of ammonia/methane mixtures at elevated pressures**
12:00 – 12:10	**Conference Photo** (in the front of the lecture hall)	
12:10	*LUNCH*	

Program

Tuesday, 10 March 2020

Session Chair: T. Kaspar

13:30 – 14:30	**Poster presentations**	
14:30 – 16:00	**Poster session** *and COFFEE*	
16:00 – 17:00	Angela Violi	**The known and unknown of nanoparticle formation in combustion and their health effects**
17:00 – 18:00	Sotiris Pratsinis	**Multiscale process design for nanoparticle synthesis**
18:00	*DINNER*	

Session Chairs and Discussion Leaders: C. Schulz, J. Janicka

19:30 – 21:30 **Panel discussion "Transformation of the energy system"**

Panelists:

- Klaus Dieterich (Innovation-Consultant)
- Zijad Lemeš (ENTEGA AG)
- Joachim Martin Paul (Bosch)
- Eberhard Umbach (KIT)
- Kurt Wagemann (DECHEMA e.V.)

Program

Wednesday, 11 March 2020

07:30	*BREAKFAST*	
08:30 – 08:45	Stefan Jorda	**About the Wilhelm and Else Heraeus-Foundation**

Session Chair: M. Pfitzner

08:45 – 09:45	Francesca Di Mare	**Large Eddy simulation of combustor-turbine interaction for innovative, decentralised power generation**
09:45 – 10:45	Heinz Pitsch	**Chemistry matters: advanced synthetic and biofuels for internal combustion engines**
10:45 – 11:15	*COFFEE BREAK*	
11:15 – 11:35	Cooper Welch	**Machine learning-based analysis of the early flame kernel in a spark-ignition engine to predict combustion performance**
11:35 – 11:55	David Escofet-Martin	**Transient thermal boundary layer development and flame wall interaction studies using 1d HRCARS and TGP in a constant volume chamber**
11:55 – 12:15	Georgios Kelesidis	**Morphology, composition and optical properties of flame-made nanoparticles**
12:15	*LUNCH*	
14:00 – 16:30	**Joint hike**	

Session Chair: H. Pitsch

17:00 – 18:00	**Poster presentations**	
18:00 – 19:00	*DINNER*	
19.30 – 21.00	**Poster session**	

Program

Thursday, 12 March 2020

07:30	*BREAKFAST*	
08:30 – 09:30	Simone Hochgreb	**Narrowing the gap between experiments and models in turbulent reacting flows**
09:30 – 10:30	Oliver Paschereit	**On our way to zero emission power plants**
10:30 – 11:00	*COFFEE BREAK*	

Session Chairs and Discussion Leaders: C. Schulz, J. Janicka

11:00 – 12:30	**Final discussion**	
12:30 – 12:45	Andreas Dreizler Heinz Pitsch	**Closing words**
12:45	*LUNCH*	

End of the seminar and departure

NO DINNER for participants leaving on Friday morning

Posters

Posters (presented on Monday)

Giovanni B. Ariemma	**Reduction of NOx emissions through water addition in MILD ammonia combustion**
Milad Bagheri	**Interface-resolving simulation of droplet impact on liquid film of the same fluids using the phase-field method**
Per-Erik Bengtsson	**On the relation between optical properties of soot and its nanostructure and composition**
Liming Cai	**Highly-automated model development for promising e-fuels from renewable electricity**
Francesca Cerciello	**Effects of pressure on lignocellulosic biomass fast pyrolysis**
Francesco Contino Xavier Rixhon	**Uncertainty quantification of energy systems**
Paulo Debiagi	**A fundamental model of char oxidation**
Mario Eck	**Novel insight of cyanuric acid hydrolysis over titanium dioxide by thermogravimetry**
Mark Fuller	**Nitrogen combustion chemistry for renewable, designer fuels**
Christopher Geschwindner	**High-speed OH-LIF of flame retarded polypropylene combined with a thermal decomposition analysis**
Kevin Keller	**Microkinetic modeling of the total oxidation of methane – understanding the water inhibition effect)**
Philippe Leick	**"Tip wetting" of gasoline injectors: Mechanism, measurement techniques, contribution to particulate emissions and mitigation strategies.**

Posters (presented on Monday)

Charlotte Rudolph	**Exergy storage in piston engines by pyrolysis of natural gas/hydrogen mixtures**
Una Trivanovic	**Effect of sodium chloride solutions on soot morphology and mixing state from a large-scale laboratory flare**
Sonal K. Vallabhuni	**Experimental and kinetic modeling studies on the auto-ignition of methyl crotonate at high pressures and intermediate temperatures**

Posters (presented on Tuesday)

Suphaporn Arunthanayothin	**Ammonia-methane interaction in jet-stirred and flow reactor: an experimentalnand kinetic modeling study**
Antonio Attili	**DNS of turbulent premixed combustion at high Reynolds number**
Ariane Auernhammer	**Characterization of jet types and wetting behavior in direct cooling system for electric motors**
Hesheng Bao	**Computational investigation of a diesel-like flame applying a flamelet-based combustion model and large eddy simulation**
Isaac Boxx	**An experimental study of hydrogen-enriched natural gas swirl flames in a gas turbine model combustor**
Jonas Fischer	**Refuse-derived fuel characterization by convective drying**
Arvind Gangoli Rao	**Energy transition in aviation: the role of cryogenic fuels**
Munko Gonchikzhapov	**Reactions of $Fe(CO)_5$ $Fe(C5H_5)_2$ and TTIP as precursors for spray flame synthesis of nanoparticles during partial spray evaporation**
Jürgen Herzler	**Kinetics of partial oxidation of methane/additive mixtures for polygeneration processes: High-pressure shock-tubes experiments**
Dmitrii Kliukin	**Spatiotemporal coherent anti-stokes Raman spectroscopy in the recirculation zone of bluff-body stabilized premixed methane/air flames**

Posters (presented on Tuesday)

Christian Kuntz	**Modelling urea deposit formation and decomposition on SCR catalysts**
Tao Li	**Investigation of solid fuel particle group combustion using volumetric OH-LIF imaging and diffuse backlight-illumination**
Gauthier Limpens	**The role of renewable fuels in low-carbon societies**
Yihua Ren	**Flame synthesis of carbon metal-oxide nanocomposites in a counterflow burner**
Dominik Schmidt	**Experimental assessment of the release of Nitrogen, Sulfur and Chlorine species during pyrolysis of coal and biomass in CO_2 atmosphere**
Bo Shu	**Experimental and modeling study on the auto-ignition properties of ammonia/methane mixtures at elevated pressures**
Yalin Wang	**Numerical simulation and experimental research of biomass and coal coupled combustion**
Johannes Wenz	**Pyrolytic reactions of methyl formate: Shock-tube studies and kinetic modeling**

Posters (presented on Wednesday)

Davide Amato	**On the “anhysteretic state” of MILD combustion process**
Kai Banke	**Polygeneration by partial oxidation of fuel-rich Methane/air mixtures in an HCCI engine – Different approaches to achieve auto-ignition**
Rob Bastiaans	**Energy transition combustion research & challenges: Eindhoven activities**
Carina Büchner	**Transition metal borides as electrocatalysts: State of the art and first investigations of the activity of iridium boride**
David Escofet-Martin	**Transient thermal boundary layer development and flame wall interaction studies using 1d HRCARS and TGP in a constant volume chamber**
Mustapha Fikri	**Kinetics study of dimethoxymethane in shock tube: Experiment and modeling**
Annunziata Forgione	**A novel approach to methanol production: integration of solar hydrogen, chemical looping combustion and syngas production via reverse water gas shift reaction**
Jinlin Han	**Experimental investigation of ethanol/diesel dual-fuel combustion in a heavy-duty diesel engine**
Tina Kasper	**Mass spectrometric study of iron- and silicon-containing hydroxides and oxides in particle forming flames**
Georgios Kelesidis	**Morphology, composition and optical properties of flame-made nanoparticles**
Domenico Lahaye	**Reducing emissions of industrial furnaces: Two case studies in the port of Rotterdam**

Posters (presented on Wednesday)

Maria Virginia Manna	**Identification of combustion regimes for highly diluted NH3/O2/N2 mixtures in a jet stirred flow reactor**
Francesco Saverio Marra	**Numerical approaches for analysis, reduction and validation of detailed chemical mechanisms of new generation fuels**
Marcel Richter	**Spectral modeling of an oxy-fuel pulverized coal fired boiler considering non-gray gas and particles**
Lea Totzauer	**Cerium phosphates as potential luminescent oxygensensing materials at elevated temperatures**
Cooper Welch	**Machine learning-based analysis of the early flame kernel in a spark-ignition engine to predict combustion performance**

Abstracts of Talks

(in chronological order)

Combustion perspectives: Some contributions from physical chemistry

K. Kohse-Höinghaus[1]

[1]Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany

The quest for cleaner air, the threats of climate change, and the according transformation of the energy system are foremost issues in a more sustainable development. Combustion of fossil fuels is increasingly regarded as a problematic technology, and many countries have set goals towards a more significant share of renewables. Combustion science today must thus reach beyond its classical role. Combustion processes with a lower carbon signature and reduced emissions, relying on new system approaches and alternative fuels, are being developed, while on the larger scale, process integration is desired in a future energy perspective. The lecture will give some examples of current combustion chemistry and diagnostics research, including low-temperature combustion, alternative fuels, and pollutant formation, and it will aim to provide food for discussion on the perspectives of combustion research.

Waste derived fuels: significance, challenges, solutions

V. Scherer[1]

[1]Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum Germany

Heraeus seminar on Fuels, Processes, and Combustion Physics in the Energy Transformation

The United Nations expect that in 2050 more than 2/3 of the world population lives in large cities (today 50%). The number of megacities with more of 10 million inhabitants is expected to rise from 28 to 41. In parallel, the quantity of domestic and industrial waste is expected to increase too, driven by this development. According to forecasts the total amount of waste will roughly double until 2050.

Although recycling has become increasingly important, in particular in highly developed countries, there still is the need of thermal disposal of waste or the thermal utilisation in waste to energy plants from domestic and industrial sources. The potential to use such fuels as a source of energy is significant. Although on a world-wide scale in the order of 4500 waste incineration plants exist, landfills are still prevalent even in highly developed countries like the US.

The current contribution will give an introduction into the potential and use of waste derived fuels. The combustion of these fuels and the theoretical description of their conversion is difficult, because the fuel broadly varies in size, shape and chemical composition. Hazardous components like chlorine may be contained. Waste to energy plants, which are mainly based on grate firing systems, allow a long proven direct thermal utilization and at the same time significant volume reduction of the material to be disposed. Details on the available theoretical/numerical descriptions applicable for their design and optimization will be given. Another form of waste material is refuse derived fuel (RDF), a pre-treated fuel essentially produced from domestic and industrial waste, which includes biodegradable material as well as plastics. This can be can be used for co-combustion in pulverized fuel boilers or in cement plants. RDF fuel particles can be transported pneumatically and, hence, appropriate models for their flight trajectories within the respective conversion devices are required for design and optimization. An approach to model the combustion of these fuels will be introduced. Finally, some examples of other residues from industrial processes to be thermally treated will be shortly discussed.

Piston Engines for Polygeneration

B. Atakan[1]

[1]University of Duisburg-Essen, Thermodynamics / IVG, Lotharstraße 1, 47057 Duisburg, Germany

Natural gas and biogas are both consisting of large amounts of methane and are predominantly used for energetic usage, while around 5 % are used for chemical conversion in chemical industry. The methane usage will continue for many years to come, while both conversions take place with non-optimal efficiencies. One approach to overcome these low efficiencies is to use piston engines as chemical reactors for a combined production of work, heat, and useful chemicals like syngas (H2/CO) or acetylene. Such a polygeneration process is quite fuel rich, and thus, due to low flame speeds, a kinetically controlled homogeneous charge compression ignition process (HCCI) is preferable. This leads to the problem that methane is quite inert and measures are needed to ignite it after compression. High initial temperatures, high compression ratios, or different additives can help to overcome the inertness and can lead to ignition in such engines. These systems were analyzed with respect to the chemical kinetics, the thermodynamics, and the exergo-economics; in addition concepts for energy recuperation and product separation were developed and analyzed. In total, it is found from theory and from experiment that the combined process is in many cases preferable in comparison to separate processes for energy conversion and chemical conversion, but some challenges remain, like the relatively high amounts of additives needed for ignition. The concept can be expanded further towards using the piston-cylinder system as a compressor to convert mechanical energy in endothermal reactions to chemical energy for chemical energy storage, as will be explained.

Results and ideas from several cooperation partners within the DFG research unit 1993 'Multifunctional conversion of species and energy' will be presented.

Uncertainty quantification of energy systems

Francesco Contino[1], **Xavier Rixhon**[1], **Gauthier Limpens**[1], **Kevin Verleysen**[2,3], **Diederik Coppitters**[2,3,4], **and Hervé Jeanmart**[1]

[1]Institute of Mechanics, Materials and Civil Engineering iMMC), Université catholique de Louvain (UCLouvain), Place du Levant, 2, 1348 Louvain-la-Neuve, Belgium
[2]Fluid and Thermal Dynamics (FLOW), Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium
[3]Combustion and Robust Optimization Group (BURN), VUB and ULB, 1050 Brussels, Belgium
[4]Thermal Engineering and Combustion Unit, UMONS, Place du parc 20, 7000 Mons, Belgium

The energy transition involves many uncertainties. When designing energy systems, we need to include those uncertainties if we want to make informed and meaningful choices. Still there are three main issues: for large complex systems, the number of parameters becomes overwhelming leading to the well-known *curse of dimensionality*; for dynamic systems, uncertainties will have a compound effect—accumulating in time; and most of the time, we have an unclear definition of uncertainties—we cannot distinguish between natural variation and uncertainty related to a lack of knowledge. We tackle these three challenges: by applying sparse polynomial chaos expansion (PCE) for the uncertainty quantification (UQ) of the energy system of a country [1], by implementing time-dependent PCE for the dynamic production of ammonia [2], and by using a new formulation of uncertainties—imprecise probabilities—for hydrogen production [3]. Based on these three examples, this presentation will give an overview of the techniques we are developing. The results show that the information within the uncertainties provides insight for the designer or the decision maker. In the case of the national Belgian energy system, we applied the method to a large amount of uncertain parameters (more than 200). The impact on the total energy system cost shows that only few critical parameters drive the impact. In the case of the sensitivity analysis on the dynamic production of ammonia, operational and parametric uncertainties significantly affect the system's performance over time. In an optimization framework, including the knowledge we have on the uncertainties provides the designer with robust design alternatives. Obtaining those efficiently however is still ongoing research.

References

[1] Limpens, G., Jeanmart, H., & Maréchal, F. (2020). Belgian Energy Transition: What Are the Options?. *Energies*, *13*(1), 261
[2] K. Verleysen, D. Coppitters, W. De Paepe, A. Parente, F. Contino, Fuel 266, 117049 (2019)
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Highly-automated model development for promising e-fuels from renewable electricity

L. Cai and H. Pitsch

Institute for Combustion Technology, RWTH Aachen University, 52056 Aachen, Germany

Carbon-neutral synthetic fuels, which can be produced from renewable electricity by the hydrogenation of carbon dioxide captured from air or exhaust gas, are attracting growing interest from both academic research and industry due to their positive impact on the overall CO_2 balance. The catalytic conversion of carbon dioxide opens various new possibilities to produce fuel species with more complex molecular structures and tailored physical and chemical properties, for which a deep understanding of the underlying combustion kinetics in form of a chemical mechanism is often missing. Therefore, the rapid generation of accurate chemical mechanisms is of high interest for these promising e-fuels.

This work combines advanced automatic model generation, optimization, and reduction methods to facilitate a rapid kinetic model development. The methodology is demonstrated by generating a chemical mechanism for the promising class of synthetic e-fuels oxymethylene ethers (OMEs) [1], which exhibit good auto-ignition characteristics for compression-ignition engine applications. An initial model is derived using an automatic reaction class-based mechanism generator. To ensure the chemical validity of the mechanism, the automatic generator applies the same reaction classes and rate rules consistently for OME_{2-4}, which are adopted from a recently published OME_1 mechanism [2]. For improved model prediction accuracy of ignition delay times, the mechanism is then optimized automatically using the method of Ref. [3] by calibrating the rate rules within their uncertainties against experimental target data of all OME fuels. To reduce the computational effort of, for instance, computational fluid dynamics simulations, the detailed mechanism is finally reduced to a skeletal level using a multi-stage reduction strategy [4]. It is shown that this highly automated model development process is able to provide accurate chemical mechanisms with compact model size in a very efficient manner for e-fuel components of interest.

References

[1] L. Cai et al., Fuel 264 116711 (2020).
[2] S. Jacobs et al., Combustion and Flame 205 522-533 (2019).
[3] L. Cai, H. Pitsch, Combustion and Flame 161 405-415 (2014).
[4] P. Pepiot-Desjardins, H. Pitsch, Combust. Flame 154 67-81 (2008).

A fundamental model of char oxidation

P. Debiagi[1], **A. Locaspi**[2], **C. Hasse**[1] **and T. Faravelli**[2]

[1] *Simulation of Reactive Thermo-Fluid Systems, TU Darmstadt, Darmstadt, Germany*
[2] *Department of Chemistry, Materials and Chemical Engineering "Giulio Natta",*
Politecnico di Milano, Milan, Italy

A detailed fundamental description of char oxidation is currently under development. The aim is to lay the groundwork for the development of a comprehensive model of solid fuel combustion. The present model addresses char produced by complete pyrolysis. In the present study, a "completely pyrolyzed" fuel is assumed if no release of volatile species occurs when pyrolyzed a second time. This condition can be inferred both from experiments and pyrolysis models, supported by the resulting zelemental composition of the produced char. Physical and chemical phenomena during pyrolysis is accounted, allowing to describe the initial structure of the char particle. A three-phase assumption is employed to describe char oxidation. The chemical reaction mechanism proposed was developed by analogy to gas-phase reactions, obtaining a detailed approach for char conversion. The model can be extended for all carbonaceous materials taking into consideration their particularities in physical and chemical properties.

Controlling the emissions of internal combustion engines: Current status and future challenges

O. Deutschmann[1]

[1]Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany

Controlling the emissions of internal combustion engines has been one of the major challenges for research and development in the mobility, transportation, and energy sectors for many decades. Today, complex after-treatment systems often containing several of different devices such as oxidation catalysts, three-way catalytic converters, SCR-catalysts, dosing systems for reducing agents, NOx-storages-reduction catalysts, ammonia slip catalysts, and particulate filters, reduce most of the pollutants from the exhaust gases, in particular unburnt hydrocarbons, aldehydes, CO, NOx, and soot. The emission control systems with their continuously varying inlet and boundary conditions are meanwhile very dynamic and complex small chemical plants. However, further improvements are needed due to lower legislative emission limits, alternative fuels, and more efficient engine concepts leading to less CO2 but more NOx emissions.

This contribution provides an overview on the state-of-the art exhaust-gas after-treatment devices for on-road, off-road, and stationary applications of internal combustion engines. Current and future challenges of emission control will be discussed such as controlling of emissions of the greenhouse gases methane and N2O, cancerogenic compounds such as HCHO and further reduction of NOx emissions.

Towards a better understanding of Reactive Thermofluidics in I.C. Engines - Potential and Limitations of Direct Numerical Simulation

C. Frouzakis, Y. M. Wright, G. Giannakopoulos, K. Boulouchos[1]

ETH Zürich, Aerothermochemistry and Combustion Systems Laboratory, Zürich, Switzerland

Internal Combustion Engines are expected to still play a relevant role in the future energy system, particularly in long-haul, heavy duty transportation in combination with synthetic renewable fuels for decarbonization. Therefore, turbulent-thermochemistry interactions need to be understood in depth, also for such fuels, through both non-intrusive experiments and advanced simulation methods. This applies also to multi-mode, multi-fuel engine combustion processes under specific consideration of the transient character of ignition and flame propagation including near wall phenomena.

Direct Numerical Simulation has recently emerged as promising method in order to shed light into phenomena so far not accessible by either LES or measurements. Despite inherent limitations due to enormous computational requirements for real-world applications, use of DNS can be targeted to support development of improved submodels in RANS/LES algorithms synergetically with advanced laser-based diagnostics. In the talk we will give examples of recent progress in understanding flow field, heat transfer and unsteady premixed flame propagation in some canonical engine-like set-ups.

Thermal annealing of coal and biomass: from combustion science towards new carbon materials

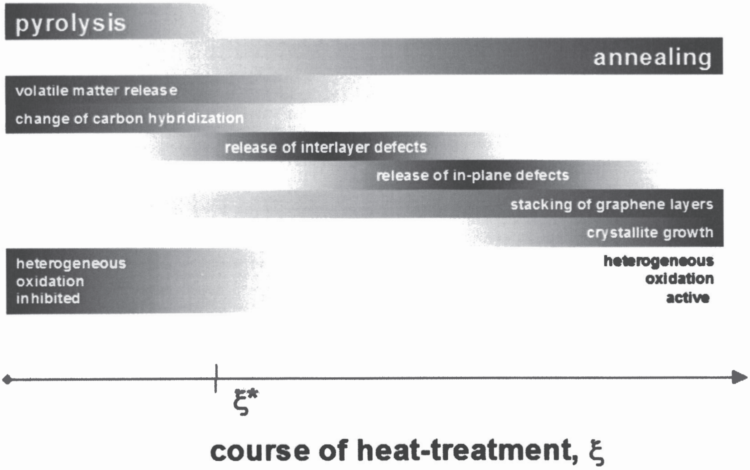
O. Senneca[1]

[1]*Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, P.le Tecchio 80, 80125 Naples, Italy*

During the lifetime of coal and biomass particles in a reactor severe changes in carbonaceous structure occur. In the early stages of heat treatment, transformations at both the structural and chemical level are accompanied by volatile matter release and well recognized in the combustion literature under the name of pyrolysis. Prolonged heat treatment, even in parallel with heterogeneous reaction, produces further changes in the carbonaceous structure, which include release of interlayer and in plane defects, stacking of graphene layers and crystallite growth. These phenomena are recognized in the literature under the name of Thermal Annealing.

Within the context of combustion science a large body of literature explored coal annealing and shed much light on the effects of heat treatment on the char reactivity, especially in the late stages of burn-off. Thermal annealing of biomass has been neglected or underestimated in the context of combustion science, on the contrary the effects of heat treatment, often combined with chemical treatments, on the structure of lignocellulosic materials, have been investigated in the context of material sciences. The goal in this case was to produce green graphene like materials.

The present talk will address thermal annealing of coal and lignocellulosic materials, looking at both the reactivity and the structural issues and trying to bridge the concepts developed in combustion and in material science.



Large Eddy Simulation of turbulent combustion in Gas Turbines

B. Cuenot[1]

[1]CERFACS, 42 Avenue Gaspard Coriolis, 31057 Toulouse Cedex 1

Large Eddy Simulation (LES) is now recognized as a powerful numerical approach to address complex problems, such as turbulent reacting flows. LES is able to provide reliable predictive solutions of both academic and real industrial systems, and gives new insight into the underlying physical phenomena. Moreover, to alleviate some uncertainty associated to boundary conditions, LES can be coupled to other solvers to include complementary system elements and physics in the computation.

In the case of gas turbines, many different and complex physics must be described and coupled. This includes turbulence, chemistry, heat transfer, two-phase flows and phase change when the fuel is liquid, solid particles dynamics and chemistry for soot prediction, or acoustics to study combustion instabilities. Non-linearity, associated to a wide range of space and time scales, make the full resolution of turbulent combustion not affordable, and modelling is necessary. Models must be efficient, accurate and reliable, and also describe the interactions between the various physics.

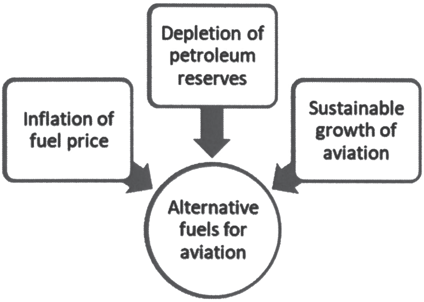
In the lecture an overview of the physical models used for LES of turbulent combustion will be first given, focusing on the most recent and successful approaches. This will be followed by examples of application to aeronautical gas turbines, addressing a variety of issues such as ignition, instabilities, heat transfer or pollutant emissions. Comparison with experiments and results analysis will allow to demonstrate the capacity of LES and coupled multiphysics to tackle complex problems with accuracy and efficiency.

Energy transition in aviation: the role of cryogenic fuels

Arvind Gangoli Rao[1]

[1]Delft University of Technology, Delft, The Netherlands

Aviation is the backbone of our modern society. At present, around 4.5 Billion passengers travel through the air every year and aviation is responsible for around 5 % of anthropogenic causes of Global Warming [1]. With the increase in global GDP, the number of travellers is expected to increase to 7.5 Billion by 2037 and to around 15 Billion by 2050. Whereas surface transportation systems are able to reduce their CO_2 footprint, thanks to the increased use of electric / hybrid vehicles, the aviation sector is restricted in the energy source. Currently, aviation consumes around 1.1 Billion litres of Jet Fuel every day and is poised to increase by 3% every year, despite the improvements in aircraft efficiency. The main drivers for alternative fuels are shown in the adjoining figure.



While there are high hopes on biofuels, there are some serious challenges which include; scaling of production, fuel consistency, availability of biomass, conflict with the food chain, high price, competition with surface transport, unavailability of subsidies in aviation, etc. Therefore biofuel can be a part of the solution but not the solution itself.

In this talk, I will explore the viability of alternatives like Hydrogen and Liquefied Natural gas (LNG) for aviation. The talk explores various designs/routes in which these fuels can be used for civil aviation in the future.

References

[1] Lee, D.S., Fahey, D.W., Forster, P.M., Newton, P.J., Wit, R.C.N., Lim, L.L., Owen, B., Sausen, R., “Aviation and global climate change in the 21st century”, Atmos. Environ. Vol. 43, 3520–3537, 2009

[2] Airbus, Growing Horizons 2017/2036, Airbus, Toulouse, France, 2017

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An Experimental Study of Hydrogen-Enriched Natural Gas Swirl Flames in a Gas Turbine Model Combustor

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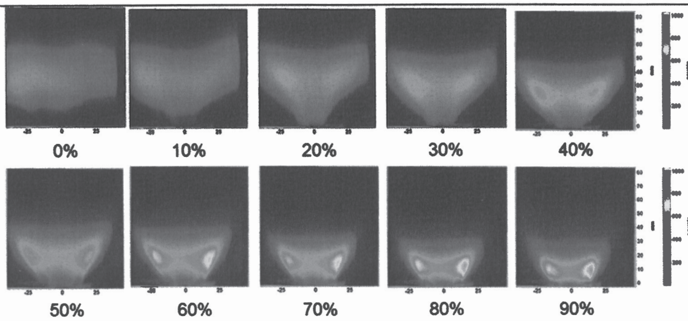
Lean, methane-air flames in a technically premixed, swirl stabilized burner (based on the PRECCINSTA geometry) were studied at operating conditions spanning several thermal powers and equivalence ratios with hydrogen admixtures of up to 90% (by volume). The PRECCINSTA burner has previously been studied both experimentally and computationally [1-4] and represents an excellent test case for exploring the effect of hydrogen on technically premixed swirl flames.

The flame shape and combustion instability characteristics were studied using time-resolved (10 kHz) OH* chemiluminescence imaging and two-microphone acoustic measurements. The stable and unstable operating conditions are experimentally characterized in terms of equivalence ratio and thermal power, and the peak frequencies and amplitudes of thermoacoustically excited cases are measured. This work finds (as expected) that hydrogen addition significantly affects the flame shape and combustion instability limits. Specifically, the flame is made more compact and the flame is observed to change from M to V-shaped at fuel lean conditions, both of which impact combustor thermal loading. Furthermore, hydrogen addition raises the peak frequencies and modifies the thermoacoustic amplitude.



0% 10% 20% 30% 40%

50% 60% 70% 80% 90%

Figure 1 – OH* Chemiluminescence showing the mean flame shape of one series of methane-air flames with increasing admixtures of hydrogen. L_{th} = 15kW, $\phi = 0.65$.

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Experimental and modeling study on the auto-ignition properties of ammonia/methane mixtures at elevated pressures

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The present worldwide concern about global warming has stimulated the development of carbon neutral energy technologies to mitigate the need of fossil fuels and the emission of greenhouse gases. In this sense, ammonia (NH_3) is regarded as one of the most viable alternatives to produce carbon-free energy, presenting high energy density and ease of storage and handling. However, its low flammability and high NO_x emission potential inhibit the implementation of pure NH_3 in these systems [1]. Methane on the other hand is a favorable low emission fuel and can be used as a co-firing fuel in ammonia combustion to promote the reactivity and control the emission levels [2,3]. However, knowledge of the ignition properties of NH_3/CH_4 mixtures at intermediate temperatures and elevated pressures is still scarce.

This study reports ignition delay times of $NH_3/CH_4/O_2$ mixtures diluted in Ar or Ar/N_2 over a temperature range of 900-1100 K, pressures of 20 and 40 bar, and equivalence ratios of 0.5, 1.0, and 2.0. The results demonstrate that a higher CH_4 mole fraction in the fuel mixture increases its reactivity, and that the reactivity decreases with increasing the fuel-oxygen equivalence ratio. Most recent mechanisms of Glarborg et al. [4] and Li et al. [5] were compared against the experimental data for validation purpose. Both mechanisms can predict the measurements fairly well. Detailed modeling for emissions indicated that adding CH_4 to the fuel mixture increases the emission of CO and NO_x. Moreover, addition of CH_4 complicates the reaction pathway of both CH_4 and NH_3 consumptions due to the cross reaction between carbon and nitrogen radicals.

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The known and unknown of nanoparticle formation in combustion and their health effects

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Accurate simulations of reactive systems present foremost challenges to both our fundamental understanding and computational modeling capabilities. The chemistry underlying combustion stems from a complex nonlinearly coupled network of tens of thousands of reactions across order-of-magnitude variations in temperature, pressure, and timescale. Computational modeling creates an opportunity to develop and optimize hydrocarbon combustion through improved prediction and understanding.

Models capturing the growth of polycyclic aromatic compounds (PACs) and nanoparticles in combustion have always been faced a large degree of uncertainty due to the lack of detailed direct experimental validation. In particular, data on molecular structures, chemical composition, size, cross-linking and aliphatic chains are still very limited.

In this work we use atomistic simulations to model the formation of PACs in combustion conditions, providing information on the chemical and structural evolution of these compounds. Looking at data reported in the literature, we analyse flames that have been experimentally characterized in terms of mass spectra and other molecular properties and embark in a comparison based on molecular structures, and extend to other properties of the PACs. The simulation results demonstrate that our in-house code, SNapS2, is able to capture the vast array of PACs in terms of a large variety of functional groups and mass distributions providing confidence in the code.

Network analysis are carried out to analyze the reaction pathways in various conditions and report on the relative importance of the growth mechanisms.

To further assess the impact of combustion by-products, we investigate the effect of molecular structure and chemical composition on human cell membranes using molecular dynamics simulations. Results show the relative importance of particle characteristics and the effect on various types of cells.

Multiscale Process Design for Nanoparticle Synthesis

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Recent advances in understanding of aerosol formation and growth through computational fluid-particle dynamics and discrete element modeling and molecular dynamics allow now optimal reactor design, away from the Edisonian approaches of the past. This leads to scalable synthesis of sophisticated nanoparticles with controlled composition, size and morphology resulting in high value products (nanosilver and carbon-coated Co nanoparticles) in the market already, while several promising ones are emerging such as single atom catalysts and breath sensors for monitoring body fat burning and even detecting methanol poisoning in liquors (1).

This lecture will highlight first the significance of the high temperature particle residence time concept in computational fluid-particle dynamic models as exemplified in particle formation by flame spray pyrolysis. Then the power of discrete element models in depicting the detailed morphology of combustion-generated particles will be elucidated with titania, silica or soot formation (2). Finally the elegance of molecular dynamics coupled with experimental validation in detailing how surface diffusion dominates the early stages of coalescence of titania, silver and gold nanoparticles or how silver occupies preferentially the surface of its nanoalloys with gold or how agglomerates of polydisperse primary particles settle faster than those with monodisperse will be elucidated as time permits it (3).

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Large Eddy Simulation of Combustor-Turbine Interaction for innovative, decentralised power generation

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Small- to medium-sized (<30 Mw) gas turbines can be conveniently employed for decentralised power generation in conjunction with power cycles based on renewable sources, such as, for example the power-to-X technologies. The envisaged devices should be able to deliver the required output at short notice (peak coverage) and utilise a variety of fuels with possibly different LHV. Hydrogen-based combustion processes are especially attractive for the enormous potential of reducing virtually to zero CO2, however the design and control of gas turbines which satisfy the requirement of stability and efficiency, hence rendering hydrolysis-based cycles economically viable and safe, poses remarkable challenges, particularly regarding the prediction of the (unsteady) temperature distribution at the inlet of the high-pressure turbine. Whilst industrial gas turbines are the natural candidates for such purposes, design improvements of the coupled combustion and expansion components inspired by modern aeroderivatives are necessary to reach the required efficiency. The prediction of the interaction between the main flow and the cooling system at the exit of the combustion chamber is of paramount importance for a flexible and yet safe design. In this work we present the latest developments and application of the in-house, high-fidelity simulation method to the prediction of the temperature and mixing patterns at the exit of the combustor of a small- to medium-size gas turbines under unsteady operation. Special attention has been paid to the development of synthetic boundary conditions for the combustor-turbine interface considering also the scalar turbulent fluctuations.

Chemistry Matters: Advanced Synthetic and Biofuels for Internal Combustion Engines

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Machine learning-based analysis of the early flame kernel in a spark-ignition engine to predict combustion performance

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The understanding of the sources of cycle-to-cycle variations (CCVs) in spark-ignition (SI) engines is critical in optimizing engine performance and reducing pollution. Variations of in-cylinder motion are regarded as important sources of engine CCVs and are unavoidable due to the nature of turbulent flows. However, through a better understanding of the processes involved in the interaction between engine flows and early flame CCVs, significant improvements in engine efficiency can be realized.

Engine performance in an optically accessible single-cylinder SI engine is investigated by means of machine learning (ML) analysis of planar Mie scatter images of the early flame (7.2 crank angle degrees after ignition) and the cycle maximum pressure (P_{max}). After a binary classification of cycles with high (HC) and low (LC) P_{max} based on a median threshold of 34.6 bar, the dataset of 615 cycles is carefully evaluated to select 32 flame features as input parameters for the ML analyses. Different decision tree (DT) -based supervised ML methods are used to test the accuracy of the prediction of cycles with HC or LC. In order to train and test all ML methods, a nested cross-validation (CV) technique along with a grid search with 10-fold CV on each inner-fold is used. This technique outputs the mean and standard deviation of the outer models' accuracies as well as the mean feature importance. In addition, the feature space is reduced by selecting a subset by hand and by using the first 10 principal components of a principal component analysis.

All ML methods yielded a prediction accuracy of at least one standard deviation above chance level ($p_{\text{chance}} = 50\%$), with the most accurate being the logistic regression model and hand-selected subset (65%). The probability of the burned gas occurring to the left of and below the spark plug is much greater in HC cycles than in LC cycles. This initial analysis is confirmed by the CV feature importances, which show that two features, the value of the x-coordinate of the leftmost and bottommost positions, are by far the most significant in predicting cycles of HC. Machine learning models were then tested with the logistic regression method with these two features only. This standalone model yielded a prediction accuracy of about 60% which means that even with such limited information as the leftmost and bottommost position of the 2D cross-section of the early flame at one point in time, CCVs can reasonably be predicted. Using such a reduced standalone model, more complex features such as flow velocities and spark energies can be implemented in the future to gain further insight into the underlying mechanisms behind engine CCV.

Transient thermal boundary layer development and flame wall interaction studies using 1d HRCARS and TGP in a constant volume chamber

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Unburned hydrocarbon emissions (UHC) are an important contributor to greenhouse gas emissions. Near-wall transient heat transfer and flame-wall interaction (FWI) are topics of great importance in understanding emissions in downsized internal combustion (IC) engine and gas turbine technology. This talk describes simultaneous measurements using 1D hybrid fs/ps rotational CARS (HRCARS), thermographic phosphors (TGP) and CH* imaging performed in an optically-accessible constant volume chamber designed to study transient near-wall heat transfer processes and FWI. HRCARS provides single-shot gas-phase temperatures, while thermographic phosphors measures wall temperature and CH* provides insight regarding the flame front position. The simultaneous measurements are used to resolve thermal boundary layer (TBL) development and the associated gaseous heat loss for three important processes occurring in IC engines: (1) an unburned-gas polytropic compression process, (2) FWI, and (3) post-flame, gas expansion, and cooling processes. During an unburned-gas mild polytropic compression process, measurements show a small wall heat flux (≤ 5 kW/m^2) that yields to an appreciable temperature stratification through a developing TBL, with adiabatic compression in the core gas and polytropic compression near the wall. During FWI, gases closest to the wall ($y < 0.2$mm) continue to experience thermal loading from polytropic compression until the flame is within ~1.4 mm from the wall. Immediately afterwards, the wall first senses the flame as wall temperatures begin to increase. The thermal profiles support the understanding of an unburned thin layer of fuel close to the wall. During FWI, gas temperatures up to 1150 K impinge on the wall, producing peak wall heat fluxes (620 kW/m^2) and prompting an increase in wall temperature ($\Delta T = 14$ K). Gaseous heat loss in the post-flame gas occurs rapidly at the wall, yielding a TBL of colder gases extending from the wall as wall heat flux slowly decreases.

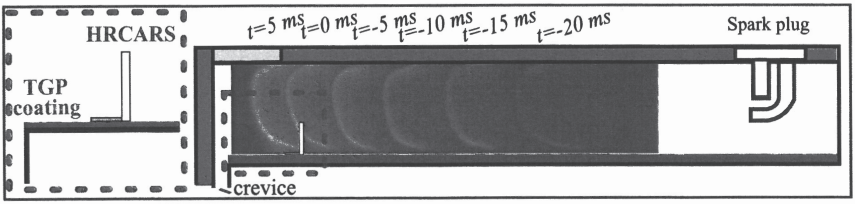

Figure 1. *Experimental setup for the combined 1D-HRCARS, TGP AND CH*.*

Morphology, composition and optical properties of flame-made nanoparticles

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Climate change has been identified as "one of the greatest challenges of our time" [1]. New policies must be implemented to limit the temperature increase below the 1.5 or 2 °C above pre-industrial levels following the recent Paris Climate Agreement. Most importantly, new technologies for the removal of long-lived CO_2 emissions from the atmosphere need to be developed and scaled-up to attain the above limits by 2050. Unlike CO_2 emissions that have an atmospheric lifetime of more than 1000 years, soot is a short-lived atmospheric pollutant with a lifetime of about 7 days. So, reducing soot emissions could have an immediate impact on global warming, delay climate effects induced by CO_2 and "buy" significant time for implementation of new technologies for reduced CO_2 emissions. In this regard, quantifying the impact of soot morphology and composition on its optical properties is essential for monitoring of soot emissions from different combustion sources and the accurate estimation of the climate impact of soot.

Here, this understanding is advanced by discrete element modeling (DEM) of soot surface growth, aggregation [2], agglomeration [3] and oxidation [4] along with rigorous comparison to experimental data at various combustion conditions from different laboratories. The DEM-derived agglomerates are coupled with the discrete dipole approximation (DDA) to account for soot morphology and composition revealing the evolution of its light absorption [5] and scattering [6] during combustion in premixed flames. This DEM-DDA algorithm can be readily used for advancing soot optical diagnostics, as well as for a more accurate estimation of the climate impact of soot.

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Narrowing the gap between experiments and models in turbulent reacting flows

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Benchmark experiments in reacting flows are designed and used to anchor and focus modelling efforts, isolating phenomena which highlight particular features of turbulent reacting flows. In this overview we discuss how experiments are designed for the step-wise validation of turbulent combustion models, from gas phase jet diffusion flames to spray flames and practical geometries, focusing primarily on statistically steady state experiments. We survey the field and highlight a few examples where models have clearly succeeded, identify areas where significant progress is being made, and pinpoint a number of issues that are still far from being resolved, both in simple areas of turbulent premixed combustion into the much more difficult fields of turbulent spray combustion, soot formation, and unsteady phenomena of flame propagation and instabilities.

An increasingly close relationship between experiments and model using data assimilation and data mining can help unravel the physics of phenomena, point the way to the design of experiments, and provide boundaries for error and uncertainty quantification.

On our way to zero emission power plants

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Chair of Fluid Dynamics, Hermann-Föttinger-Institut
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Future energy generation and storage needs to be highly efficient and carbon free, to address climate change, but still has to be affordable. For gas turbine engines this requires the use of advanced cycles with different requirements on the combustion process. In addition, we need to address the use of different fuels, such as from biomass gasification or pure hydrogen produced using excess energy from renewable sources by electrolysis, stored, and then converted in highly efficient gas turbines delivering electrical energy and heat in peak demand periods. This does not come without challenges. Hydrogen has unique combustion properties that differentiate it from traditional natural gases. They dramatically affect flame dynamics and combustion stability.

This talk will demonstrate a few possible advanced energy generation solutions, such as ultra-wet gas turbine cycles, pressure gain cycles and oxy-fuel combustion. One of the challenges in modern highly efficient combustors, combustion instabilities, will also be addressed. The high-pressure amplitudes and heat release oscillations may cause severe structural damage to combustor or engine, limit the operational envelope of modern gas turbines and may lead to higher pollutant emissions. Stability of these combustion systems is often assessed via low-dimensional network models and measured flame transfer functions, a black box representation of the complex interaction between flow, heat release and acoustics.

Better understanding of the hydrodynamic instability mode / flame interaction is obtained by using linear stability theory. The analysis shows clearly why the precessing vortex core occurs and how it may be suppressed depending on the initial conditions. In perfectly premixed flames linear stability theory explains well saturation of heat release fluctuations at higher instability amplitudes.

Abstracts of Posters

(in chronological order)

Reduction of NOx emissions through water addition in MILD Ammonia combustion

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In the framework of the recent global energy transition the intermittency of renewables sources requires the development of specific processes and technologies able to mitigate inherent RES variability, thus allowing their sustainable deployment. Among them, chemical storage offers the possibility of storing large amounts of energy for long duration and high efficiency, while ensuring easy and safe transportation and storage [1]. In this context, ammonia is increasingly considered a feasible alternative to the use of hydrogen, due to the existence of already well consolidate production technologies and distribution infrastructures. Nevertheless, exploitation of ammonia as innovative energy carrier poses some relevant challenges. The most considerable ones are related to the significant levels of NOx and narrow stability limits. The reduction of NOx emissions below the regulatory limits by after-treatment technologies is technically feasible but it reduces the advantages of ammonia and represents a major obstacle to its large scale exploitation.

An efficient technology matching these issues is represented by MILD combustion of ammonia [2]. In this context, the aim of this work is to provide an insight into identified practical issues by investigating the influence of water addition and feeding configurations on the ammonia combustion in a cyclonic flow burner. The presence of relevant amount of vaporized water is investigated with the aim to evaluate actually the achievable NOx emission reduction at increasing water amount added in premixed and non-premixed conditions. The influence of inlet parameters (inlet mixture composition and water percentage) and feeding configurations (premixed and non-premixed) were analyzed to value process performance in terms of NOx emissions and process stability. Results allowed to identify some interesting behaviors that are useful in designing practical combustion systems capable of achieving satisfying combustion quality while reducing NOx emission at an easily manageable level.

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Interface-resolving simulation of droplet impact on liquid film of the same fluids using the phase-field method

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Progresses in computational fluid dynamics (CFD) laid the foundation for a better understanding of the combustion physics. Higher combustion efficiency, flame stability, and emission reduction are achievable through detailed numerical simulations. One fundamental process to consider is the interaction of a droplet with a liquid wall film. Deposition, crown formation, and splashing occurs depending on various factors such as droplet diameter, impact velocity, and liquid film thickness. The diffuse interface method has promising potential in the areas where the sharp interface methods are not suitable, particularly when it comes to miscible fluids. This method has the ability to accurately predict the correct flow physics. To this end, droplet impact on liquid film of the same fluids is studied numerically using the phase-field method based on a diffuse interface model implemented in OpenFOAM. Understanding the droplet impact on a wall film of one identical liquid is a preliminary step towards design of combustion chambers free from pre-ignition, caused by impact of a fuel droplet on the lubricating oil film.

On the relation between optical properties of soot and its nanostructure and composition

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The characteristic properties of soot change dramatically from the incipient particles to mature particles. Thus, liquid-like particles transform to more solid ones as well as the density and C/H-ratio increases. Further the nanostructure changes from an amorphous structure to more graphitic-like, which leads to higher absorption efficiency.

In a number of studies in premixed laminar flames, it has been show that the absorption efficiency increases when the particles become more mature, see for example [1-3]. Additionally, in recent studies it is also shown that the optical band gap and absorption dispersion coefficient decreases as soot matures [4].

In addition to the flame studies, various types of soot have been generated in a propane-fueled mini-CAST soot generator for subsequent analyses. By using different operating conditions, cold soot can be produced showing large variety in its characteristic properties. The nano-structure, morphology and composition have been characterized using various diagnostics, optical as well as non-optical [5-7].

Mini-CAST soot has been produced showing characteristic properties resembling those spanning from young to mature soot in flames. The emitted soot shows a continuum of characteristic properties related to, amongst others, the temperature and residence times in flames. An increased understanding has been achieved on how the optical properties related to the nano-structure as well as an understanding on why different combustion processes give soot with different characteristics. Additionally, the various properties of soot give us an understanding of the potential and limitations of applying various diagnostic techniques for soot detection.

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Highly-automated model development for promising e-fuels from renewable electricity

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Carbon-neutral synthetic fuels, which can be produced from renewable electricity by the hydrogenation of carbon dioxide captured from air or exhaust gas, are attracting growing interest from both academic research and industry due to their positive impact on the overall CO_2 balance. The catalytic conversion of carbon dioxide opens various new possibilities to produce fuel species with more complex molecular structures and tailored physical and chemical properties, for which a deep understanding of the underlying combustion kinetics in form of a chemical mechanism is often missing. Therefore, the rapid generation of accurate chemical mechanisms is of high interest for these promising e-fuels.

This work combines advanced automatic model generation, optimization, and reduction methods to facilitate a rapid kinetic model development. The methodology is demonstrated by generating a chemical mechanism for the promising class of synthetic e-fuels oxymethylene ethers (OMEs) [1], which exhibit good auto-ignition characteristics for compression-ignition engine applications. An initial model is derived using an automatic reaction class-based mechanism generator. To ensure the chemical validity of the mechanism, the automatic generator applies the same reaction classes and rate rules consistently for OME_{2-4}, which are adopted from a recently published OME_1 mechanism [2]. For improved model prediction accuracy of ignition delay times, the mechanism is then optimized automatically using the method of Ref. [3] by calibrating the rate rules within their uncertainties against experimental target data of all OME fuels. To reduce the computational effort of, for instance, computational fluid dynamics simulations, the detailed mechanism is finally reduced to a skeletal level using a multi-stage reduction strategy [4]. It is shown that this highly automated model development process is able to provide accurate chemical mechanisms with compact model size in a very efficient manner for e-fuel components of interest.

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EFFECTS OF PRESSURE ON LIGNOCELLULOSIC BIOMASS FAST PYROLYSIS

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The present work focuses on the effects of pressure on the quality of char and primary tar produced from fast pyrolysis of lignocellulosic biomass. Heat treatment has been carried out in a heated strip reactor (HSR) at 1573 K in nitrogen at 2, 4, 8 bar, with holding times of 3 s and heating rate of 10^4 K/s. The equipment allows quenching the volatiles as soon as they are emitted from the particles and collecting them for further chemical analyses. The char samples are also collected for thermogravimetric analysis in air. The DTG curves in air of char prepared at 2 bar shows two resolved peaks. Increasing the pressure of heat treatment from 2 to 4 bar has a minor effect on char reactivity, whereas further increase to 8 bar drastically changes the char combustion patterns, and the DTG curves exhibit only one well defined peak. For all the process conditions investigated, Oxo-aromatics are the dominant species in the tar. Benzendiol prevails in the 2 bar tar, followed by oxo-aromatic compounds related to lignin structure, while PAHs are mainly present as Fluorene. When pressure increases, Phenols compounds drastically prevail, and PAHs as Anthracene and Pyrene appear.

Uncertainty quantification of energy systems

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The energy transition involves many uncertainties. When designing energy systems, we need to include those uncertainties if we want to make informed and meaningful choices. Still there are three main issues: for large complex systems, the number of parameters becomes overwhelming leading to the well-known *curse of dimensionality*; for dynamic systems, uncertainties will have a compound effect—accumulating in time; and most of the time, we have an unclear definition of uncertainties—we cannot distinguish between natural variation and uncertainty related to a lack of knowledge. We tackle these three challenges: by applying sparse polynomial chaos expansion (PCE) for the uncertainty quantification (UQ) of the energy system of a country [1], by implementing time-dependent PCE for the dynamic production of ammonia [2], and by using a new formulation of uncertainties—imprecise probabilities—for hydrogen production [3]. Based on these three examples, this presentation will give an overview of the techniques we are developing. The results show that the information within the uncertainties provides insight for the designer or the decision maker. In the case of the national Belgian energy system, we applied the method to a large amount of uncertain parameters (more than 200). The impact on the total energy system cost shows that only few critical parameters drive the impact. In the case of the sensitivity analysis on the dynamic production of ammonia, operational and parametric uncertainties significantly affect the system's performance over time. In an optimization framework, including the knowledge we have on the uncertainties provides the designer with robust design alternatives. Obtaining those efficiently however is still ongoing research.

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A fundamental model of char oxidation

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A detailed fundamental description of char oxidation is currently under development. The aim is to lay the groundwork for the development of a comprehensive model of solid fuel combustion. The present model addresses char produced by complete pyrolysis. In the present study, a “completely pyrolyzed” fuel is assumed if no release of volatile species occurs when pyrolyzed a second time. This condition can be inferred both from experiments and pyrolysis models, supported by the resulting zelemental composition of the produced char. Physical and chemical phenomena during pyrolysis is accounted, allowing to describe the initial structure of the char particle. A three-phase assumption is employed to describe char oxidation. The chemical reaction mechanism proposed was developed by analogy to gas-phase reactions, obtaining a detailed approach for char conversion. The model can be extended for all carbonaceous materials taking into consideration their particularities in physical and chemical properties.

Novel insight of cyanuric acid hydrolysis over titanium dioxide by thermogravimetry

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The global reduction of greenhouse gas emissions is of the utmost importance. Diesel engines emit greenhouse gases, but still provide a fuel-efficient way for high-energy output, especially for the heavy-duty sector. Reduction of emissions in Diesel is possible via different catalysts like the DOC (Diesel Oxidation Catalyst) and the SCR (Selective Catalytic Reduction). The SCR technology uses ammonia to prevent NO_x emission, which is not suitable for mobile engines. However, the alternative of dosing the ammonia substitute, a urea-water-solution, is problematic. The hydrolysis step during urea decomposition is slow, which subsequently leads to the formation of deposits like cyanuric acid. The cyanuric acid has the problem of not converting but rather sublimating,[1] which then travels downstream, resublimates and plugs the exhaust system. A catalyst can remove this problem.

In this work, the activity of titanium dioxide and different ZSM-5 catalysts for the decomposition and hydrolysis of cyanuric acid were investigated. First, thoroughly thermogravimetric investigations were performed to see if the gas composition alone has an impact to the hydrolysis and decomposition of cyanuric acid. However, the improvements by gas changes alone were unsatisfactory. Therefore, investigations on an exhaust-gas test setup were performed. The cyanuric acid was heated under the previous tested gas compositions. After sublimation, it could react with the catalyst placed downstream. Thus, full conversion could be achieved.

Titanium dioxide was already investigated as catalyst in the decomposition of Bernhard et al.[2] Our study emphasizes the need to use complex gas mixtures, not only model gas mixtures. When the cyanuric acid had either oxygen or water in the gas phase missing, no complete hydrolysis was achieved. Isocyanic acid was produced along with ammonia and carbon dioxide. Furthermore, thorough structural changes in the titanium dioxide bulk was observed particularly in the absence of oxygen. These changes were investigated by XRD measurements.

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Nitrogen Combustion Chemistry for Renewable, Designer Fuels

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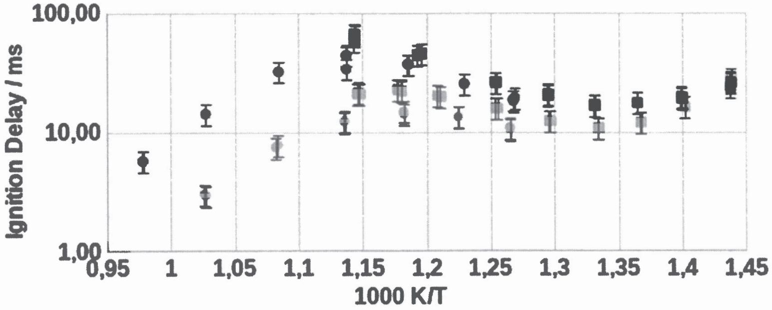
Development of renewable fuels and associated advanced combustion concepts requires advanced modeling tools for simulation. The use of exhaust gas recirculation, prompt formation of nitrogen oxides ($NO + NO_2 = NO_x$) from fuel fragments and atmospheric nitrogen, and also nitrate-based cetane enhancers in current and future engines create the possibility for significant reactions of nitrogen-containing components. Recent studies strongly suggest that current models do not accurately capture low-temperature nitrogen chemistry and fuel-NO_x interactions [1]. Further, development of biofuel combustion mechanisms require consideration of organically-bound nitrogen [2].



Experimental ignition delay times in rapid compression machine for dilute, stoichiometric n-pentane mixtures at nominal 15 bar. Black symbols are neat pentane, grey symbols are 1000 ppm NO added to mixture.

Experimental strategies include relying on n-pentane as a representative alkane fuel for establishing baseline interactions with NO_x as a detailed, well-validated model is available [3]. Further experiments will examine bio-derived fuels ethanol and ethyl acetate to expand the functional groups under consideration. Development of a mechanism to include these new interactions will also provide a framework for inclusion of interactions with other functional groups in future modeling efforts.

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High-speed OH-LIF of flame retarded polypropylene combined with a thermal decomposition analysis

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The majority of polymeric materials are combustible and therefore require tailor-made flame retardant solutions. Gas phase active flame retardants inhibit the combustion process by releasing radicals which disrupt radical chain reactions in the flame [1]. To better understand the efficacy of these chemical inhibitors, a new combination of in situ measurement techniques is applied within this experimental study [2].
The ignition and combustion of polypropylene (PP) particles is analyzed using a combination of high-speed planar laser-induced fluorescence of the OH radical (OH-LIF) and a thermal decomposition analysis. The gas phase is investigated by multiple analytical techniques to gain comprehensive knowledge on the decomposition products of flame retardants and their effect on the combustion process. Neat PP is compared with a formulation consisting of 10 wt% of a phosphorus-containing flame retardant (pentaerythritol spirobis(methylphosphonate), PSMP) which is known to provide gas phase activity. The decomposition of the neat flame retardant, PP and the flame retardant formulation is investigated using a simultaneous analysis consisting of a thermal gravimetric analysis and a differential thermal analysis device coupled to Fourier-transform infrared spectroscopy and mass spectrometry devices. By this, the release of decomposition products of the flame retardant additive can be determined. OH-LIF is used to temporally track the diffusion flame surrounding the particles during combustion in a laminar flow reactor. The radial distance to the peak reactivity zone of flame retardant containing particles increased by about 70 µm compared with neat PP particles. Tracking the peak OH signal in the diffusion flame, during ignition and the early phase of combustion, a decrease in the peak intensity is observed for flame retardant polymer particles.

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Microkinetic modeling of the total oxidation of methane – Understanding the water inhibition effect)

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Despite extensive research efforts, palladium-based methane oxidation catalysts do not keep their initial high methane oxidation activity, which is, however, of utmost importance for commercial applications. Strong inhibition and deactivation occurs particularly in the presence of H_2O. The underlying mechanism of the water inhibition effect is still not fully understood.

For this reason, PdO/Al_2O_3 powder catalysts were synthesized, characterized and tested under dynamic conditions for different concentrations of externally dosed water. The experimental results were discussed under the aspect of the impact of the gaseous atmosphere on the active noble particles and their catalytic activity. Furthermore, a modified mean-field microkinetic model with implemented surface reaction kinetics originally developed by Stotz. et al. [1], available in the software package DETCHEM [2], was used to simulate packed bed and monolith experiments. The mechanism was also implemented in the analyzing software package CaRMeN [3] to compare simulations with experimental results in an efficient way. Inhere, the model predicted trends were discussed on a molecular level with respect to available active sites for the total oxidation. Additionally, simulations were used to validate the model with profound packed bed and monolith experiments as well as to demonstrate the accuracy with experimentally obtained spatially resolved concentration profiles.

The results are of particular relevance for further modeling investigations, underlining the importance to incorporate a dynamic behavior of catalytically active particles. Future work should thus focus on further surface science investigations to ensure sufficient methane oxidation at low temperatures especially in the presence of water.

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“Tip wetting” of gasoline injectors: Mechanism, measurement techniques, contribution to particulate emissions and mitigation strategies.

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In gasoline direct injection engines with homogeneous and stoichiometric combustion strategies, particulate emissions are almost exclusively caused by liquid fuel attached to combustion chambers walls [1]. When the flame reaches these films, high temperatures and lack of oxygen can lead to formation of soot deposits on the affected surfaces. Fortunately, wetting of piston, spark plug, cylinder liner and intake valves can be minimized by adjusting the injection timing and strategy and optimizing the targeting of the spray.

Injector tip wetting – i.e. liquid fuel remaining on the tip of the injector after the end of injection – is a further source of particulate emissions. The underlying fluid dynamics are poorly understood and, while it is known that changes in injector design can lead to significant improvements in particulate emissions, no clear correlations have yet been found for all of the injector design parameters. In order to improve understanding of the relevant mechanisms and to develop models that can be implemented in 3D CFD codes, a comprehensive and detailed experimental database is needed. To this end, tip wetting is visualized using high-speed cameras and quantified using a carefully designed laser-induced fluorescence (LIF) experiment [2]. One of the most striking and consistent experimental results is a strong decrease of tip wetting and particulate emissions as injection pressure increases.

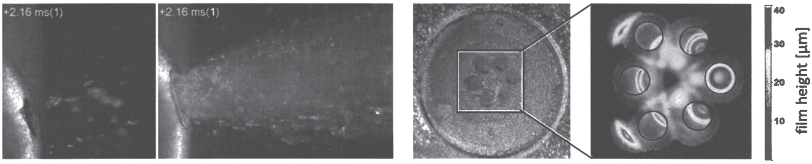

Figure 1: Visible light image of tip wetting near the end of injection for cold (left) and superheated fuel (middle left); top view of injector tip with deposits after engine run (middle right); calibrated LIF image of liquid film on injector tip after end of injection (right, superheated fuel, close up of indicated area in middle picture).

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Exergy storage in piston engines by pyrolysis of natural gas/hydrogen mixtures

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Fluctuating renewable energies and the limited range of fossil fuels motivate the increasing research on energy storage. Chemical energy storage is a long-term possibility for converting mechanical energy to chemical energy. Flexible applications to convert energy are piston engines since they are able to provide power, heat and syngas simultaneously or higher energy chemicals for energy storage purposes. In this work, the endothermal conversion of natural gas towards more valuable hydrocarbons is modelled in a piston-cylinder system. The four-stroke piston engine is a time-dependent single-zone model with detailed chemical kinetics. The Polimi elementary reaction mechanism [1] is used, which is validated for pyrolysis, partial oxidation and combustion of hydrocarbons up to C20. Due to the quasi inertness of methane at low temperatures, high temperatures are needed initiate methane conversion. These temperatures at the end of compression stroke are provided through the compression and argon dilution, which decreases the heat capacity of the mixture. The main products are hydrogen, acetylene, ethylene, ethane and benzene. The intake pressure is kept constant at 2 bar to avoid outlet pressures below atmosphere and mechanical automotive parameters are chosen in favour of the process. In particular, the compression ratio is 22 and the engine speed is 3000/min to increase the temperature at the end of the compression stroke and to decrease the reaction time. A thermodynamic analysis was conducted, considering especially the storable exergy of the product gas, exergy loss and exergetic efficiency. An additional kinetic analysis focuses on the product gas composition and the identification of the most important reactions. The process is analyzed for inlet temperatures in the range of 323-573 K and argon dilutions from 85-99%. Additionally, the effect of hydrogen addition to the natural gas/hydrogen mixture is investigated. With inlet parameters of 573 K and 93% argon, a storage power of 1.4 kW and an efficiency of 49% is achieved for 20% hydrogen in natural gas. Compared to neat methane or natural gas, the storage power and the efficiency decrease, acetylene and ethylene yields increase if hydrogen is added to the mixture.

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Effect of sodium chloride solutions on soot morphology and mixing state from a large-scale laboratory flare

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Gas flaring is a common practice in the oil and gas industry which, during hydraulic fracturing (fracking), may result in salt solutions becoming entrained in the hydrocarbon fuel. The mixing state of the resulting salt and soot particles can effect the climate impacts of the emissions through changes in optical properties or cloud forming tendencies. In this study the mixing state of salt and soot particles from a laboratory flare is examined using several methods; transmission electron microscopy (TEM), a single particle soot photometer (SP^2) and scanning mobility particle sizer (SMPS). The TEM images and the SP^2 measurements both show that the majority of soot particles were internally mixed with salt, shown in Figure 1. Meanwhile, the TEM and the SMPS show that there are a large number of salt particles on their own and that the higher the concentration of salt in the solution, the larger the resulting salt particles. A photoacoustic extinctiometer (PAX) was used in conjunction with offline, filter-based elemental carbon/organic carbon measurements to determine the mass-absorption cross-section and single scattering albedo. Both values were both unaffected by the addition of salt. No significant changes were seen in the Raman spectra. This suggests that while many of the soot particles have become internally mixed with the salt, the mixing does not have a strong effect on the optical properties of the resulting particles.

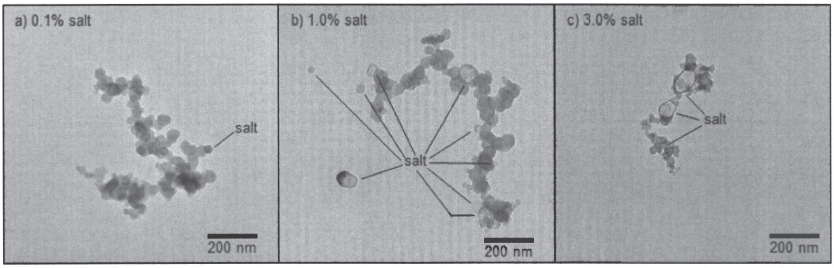

Figure 1: TEM images of internally mixed soot-salt particles from a) 0.1% salt solution, b) 1.0% salt solution and c) 3.0% salt solution.

Experimental and Kinetic Modeling Studies on the Auto-ignition of Methyl Crotonate at High Pressures and Intermediate Temperatures

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Biofuels, including biodiesel have the potential to partially replace the conventional diesel fuels for low-temperature combustion engine applications to reduce the CO_2 emission. Due to the long chain lengths and high molecular weights of the biodiesel components, it is quite challenging to study the biodiesel combustion experimentally and computationally. Methyl crotonate, a short unsaturated fatty acid methyl ester (FAME) is chosen for this chemical kinetic study as it is considered as a model biodiesel fuel. Auto-ignition experiments were performed in a rapid compression machine (RCM) at pressures of 20 and 40 bar under diluted conditions over a temperature range between 900 and 1074 K, and at different equivalence ratios (ϕ = 0.25, 0.5 and 1.0). A chemical kinetic mechanism is selected from literature (Gaïl et al. 2008) and is modified to incorporate the low-temperature pathways. The mechanism is validated against existing shock tube data [1] and the present RCM data. The updated mechanism shows satisfactory agreement with the experimental data with significant improvements in low-temperature ignition behavior. The key reactions at various combustion conditions and the improved reactivity of the modified mechanism were analyzed by performing sensitivity and path flux analysis. This study depicts the importance of low-temperature pathways in predicting the ignition behavior of methyl crotonate at intermediate and low temperatures.

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Ammonia-methane interaction in Jet-Stirred and Flow reactor: an experimentalnand kinetic modeling study

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The influence of the addition of ammonia on the oxidation of methane was investigated both experimentally and numerically. Experiments were carried out at atmospheric pressure, using a fused silica jet-stirred reactor, and a recrystallized alumina tubular reactor designed on purpose to reach temperatures as high as ~2000 K. A temperature range of 600-1200 K was investigated in the jet-stirred reactor at a residence time of 1.5 s, while experiments in the flow reactor were carried out between 1200 and 2000 K, for a fixed residence time of about 25 ms in the reactive zone. A methane/ammonia mixture, diluted in helium, was used in both reactors with equivalence ratios varied between 0.5 and 2 in the first reactor, while stoichiometric conditions were investigated in the second one. The measurement indicates that CH4 reactivity was promoted by NH3 addition below 1200 K, but not so much influence above. These results were interpreted and explained using a comprehensive kinetic model, previously validated in a wider range of operating conditions. The mechanism allowed to shed light on the underlying causes of the anticipated methane reactivity at low temperature, and of the major role played by NOx in it. This effect was shown to become less significant at higher temperatures, where the reactivity is mainly governed by H-abstractions on both fuels.

Keywords: ammonia, jet-stirred reactor, flow reactor, oxidation, detailed kinetic modeling

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DNS of turbulent premixed combustion at high Reynolds number

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A set of direct numerical simulations of turbulent premixed jet flames has been computed employing finite rate chemistry with 16 species and up to 22 Billion grid points. A methane/air mixture with equivalence ratio $\varphi = 0.7$ is employed at a pressure of 4 bar. The jet velocity is kept constant among the four cases and the jet Reynolds number, ranging from 2800 to 22000, is increased using a larger jet width.
This approach produces a set of flames with approximately constant Karlovitz number, velocity rms, and Kolmogorov scale, while the turbulence integral scale increases proportionally to the jet Reynolds number. Since real technical devices usually differ from DNS configurations due to size more than flow velocity, this scaling of the Reynolds number can be useful to extrapolate DNS results to engineering applications. A clear and conclusive scaling of the terms responsible for the flame area production is observed [1]. In particular, the statistics of the tangential strain rate are in good agreement with those for infinitesimal material surfaces in homogeneous isotropic turbulence. Once scaled by the Kolmogorov time scale, the means of both contributions to stretch, i.e., the tangential strain and the curvature term, are largely independent of location and equal across flames with different values of the Reynolds number.
It is found that the turbulent flame speed, evaluated at each streamwise position, increases with the distance from the nozzle and with the Reynolds number of the flame. This is not entirely due to the increase of the flame area since a significant thickening of the inner reaction layer, associated with negligible changes of the reaction rates, also contributes to the enhancement of the turbulent flame speed. It is concluded that, even if the flames are characterized by a constant Karlovitz number, an higher Reynolds number, and correspondingly larger turbulence integral scale, enhances the effect of turbulence inside the inner flame layer [2].
Finally, DNS of hydrogen flames in the same configuration are also considered in order to assess the effect of thermo-diffusive phenomena.

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Characterization of Jet Types and Wetting Behavior in Direct Cooling System for Electric Motors

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The current trend in automotive industry is electrification. The permanently excited synchronous machine is one possible type of an electric car motor. One of the limiting factors of electric mobility is the motor components' temperature. A possible cooling strategy for electric motors is direct cooling. Cooling fluid is injected into the interior compartment of the electric motor. Due to the direct contact of coolant and heated component surfaces, this cooling strategy aims for high and efficient heat transfer.

To study fundamentals of direct cooling an optical accessible test rig is used. This facility features successive configuration levels to resemble a permanently excited synchronous motor. The main objective of the experimental investigations on this test rig is to characterize the heat transfer between the motor components and the cooling fluid. Furthermore, the experimental results are used to improve mathematical models for numerical simulation of electric motors.

Within the test rig's limits of rotational speed, coolant flow rate and set coolant temperature, the generated jets of cooling fluid can be divided into clearly distinguishable categories. These jet types are reproducible and stationary over a wide range of operating points. The simulation results are comparable to the jet types and effects seen in the experiments.

The interaction of rotational speed, coolant flow rate, coolant temperature and jet type, which depend on the operation point of the electric motor outside the test rig, determines the cooling load and the heat transfer. Therefore, the heat transfer from the rotor to the coolant is of importance. As a first step, the wetting behavior of the coolant fluid on the rotor end disk is visualized via high-speed recordings for different operating points. Profound knowledge of the wetting behavior is important since it determines the cooling effect of the rotor end disk as well as the coolant transport to other components to be cooled.

Computational investigation of a diesel-like flame applying a flamelet-based combustion model and large eddy simulation

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Computational fluid dynamics analysis is an efficient tool to help understand the complex phenomena and explore new engine concepts. In this work, a representative diesel spray, Engine Combustion Network (ECN) "Spray A", is modeled on the frame of Dynamic Structure (DS) turbulence model coupling with Flamelet Generated Manifold (FGM). A set of recently developed turbulence models[1] is validated using the inert condition and shows significant improvement in predicting the mixing properties, which supports further studies. The new dispersion model developed for Large Eddy Simulation is applied according to Tsang's work. A variety of case studies confirm that the sub-grid scale dispersion velocity and time scale is an important issue to affect the prediction of spatial fuel distribution. Moreover, the influence of two primary model constants on both penetration and fuel distribution is found to be sensitive to mesh refinement. Besides, different combinations of dispersion and breakup model constants result in different periods for a spray to develop, while the time-averaged mixture fraction and instantaneous penetrations remain the same. This indicates that more experimental data, such as cone injection angle and spatial droplets distribution, are necessary. The reacting spray is further modeled based on the calibrated turbulence model. Strain rate is introduced into FGM as an additional dimension, as strain rate is found to be an important factor to affect the soot formation and ignition in one-dimensional flamelets created by CHEM1D[2]. The simulation is compared with various available experimental database including ignition delay, lift-off length, soot formation, rate of heat release, and shows good agreement. Strain rate is found to be a promising issue to improve the soot prediction. Analysis of detailed scatter maps proves that the new FGM application can indeed break the limitation on retrieving source terms in consequence of a prescribed single-strain-rate table for ignition delay.

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An Experimental Study of Hydrogen-Enriched Natural Gas Swirl Flames in a Gas Turbine Model Combustor

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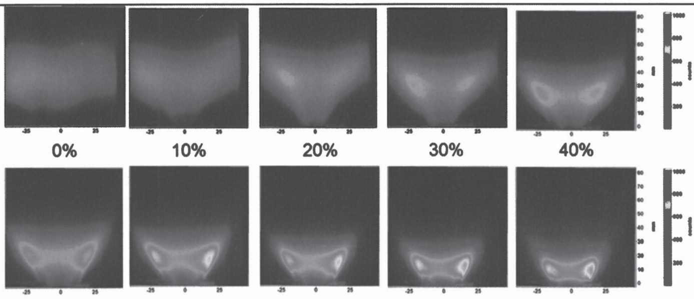
Lean, methane-air flames in a technically premixed, swirl stabilized burner (based on the PRECCINSTA geometry) were studied at operating conditions spanning several thermal powers and equivalence ratios with hydrogen admixtures of up to 90% (by volume). The PRECCINSTA burner has previously been studied both experimentally and computationally [1-4] and represents an excellent test case for exploring the effect of hydrogen on technically premixed swirl flames.

The flame shape and combustion instability characteristics were studied using time-resolved (10 kHz) OH* chemiluminescence imaging and two-microphone acoustic measurements. The stable and unstable operating conditions are experimentally characterized in terms of equivalence ratio and thermal power, and the peak frequencies and amplitudes of thermoacoustically excited cases are measured. This work finds (as expected) that hydrogen addition significantly affects the flame shape and combustion instability limits. Specifically, the flame is made more compact and the flame is observed to change from M to V-shaped at fuel lean conditions, both of which impact combustor thermal loading. Furthermore, hydrogen addition raises the peak frequencies and modifies the thermoacoustic amplitude.



0% 10% 20% 30% 40%

50% 60% 70% 80% 90%

Figure 1 – OH* Chemiluminescence showing the mean flame shape of one series of methane-air flames with increasing admixtures of hydrogen. L_{th} = 15kW, ϕ = 0.65.

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Refuse-derived fuel characterization by convective drying

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The incineration of refuse-derived fuel (RDF) accounts for up to 65 % of the thermal energy used in cement industry [1]. As RDF is different from the standard fuel of pulverized coal and may influence cement clinker quality [2], a quality control for the RDFs is important. Moisture is a directly measurable quality criterion by drying of a sample. The drying rate after evaporation of all surface moisture depends on the hygroscopicity of the materials tested (see Figure 1).
RDF contains hygroscopic (paper, cardboard) and non-hygroscopic (2D plastics, 3D plastics) fractions. The drying curve of the mixed RDF should reflect the drying characteristics of the individual fractions and allows an estimation of the RDF composition. With the experimental set-up shown in Figure 2 the drying characteristics can be measured. This also allows an assignment of moisture content to the fraction for following combustion simulations.

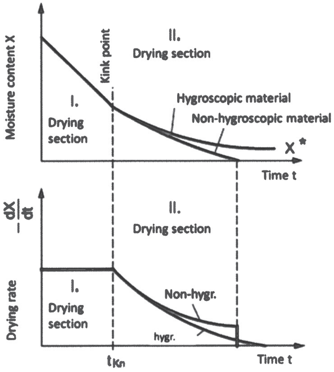

Figure 1: Drying rates for (non-) hygroscopic materials [3]

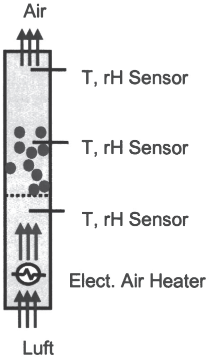

Figure 2: Experimental set-up

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Energy transition in aviation: the role of cryogenic fuels

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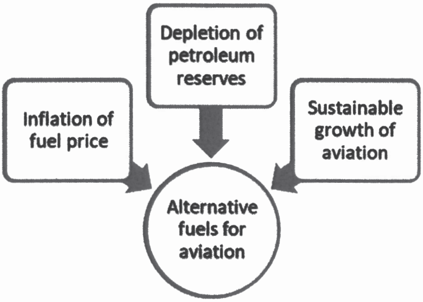
Aviation is the backbone of our modern society. At present, around 4.5 Billion passengers travel through the air every year and aviation is responsible for around 5 % of anthropogenic causes of Global Warming [1]. With the increase in global GDP, the number of travellers is expected to increase to 7.5 Billion by 2037 and to around 15 Billion by 2050. Whereas surface transportation systems are able to reduce their CO_2 footprint, thanks to the increased use of electric / hybrid vehicles, the aviation sector is restricted in the energy source. Currently, aviation consumes around 1.1 Billion litres of Jet Fuel every day and is poised to increase by 3% every year, despite the improvements in aircraft efficiency. The main drivers for alternative fuels are shown in the adjoining figure.



While there are high hopes on biofuels, there are some serious challenges which include; scaling of production, fuel consistency, availability of biomass, conflict with the food chain, high price, competition with surface transport, unavailability of subsidies in aviation, etc. Therefore biofuel can be a part of the solution but not the solution itself.

In this talk, I will explore the viability of alternatives like Hydrogen and Liquefied Natural gas (LNG) for aviation. The talk explores various designs/routes in which these fuels can be used for civil aviation in the future.

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Reactions of $Fe(CO)_5$ $Fe(C_5H_5)_2$ and TTIP as precursors for spray flame synthesis of nanoparticles during partial spray evaporation

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Spray flame synthesis is an important method of nanoparticle manufacturing. Typically, in this process a spray is introduced into a pilot flame. The heat released from the pilot flame and the burning solvent initiates the reactions of the precursors to nanoparticles in the flame. In the spray synthesis process, spray evaporation and the initial decomposition reactions of the precursor occur in the same location of the flame and at the same time. Consequently, interactions between solvent and precursor can change the intermediates in the gas phase that lead to nanoparticle formation. In this work, the thermal decomposition and the oxidation of the spray after ignition are separated by introducing the spray into an externally heated flow reactor to study the precursor solvent interaction. The thermal decomposition of the precursors $Fe(CO)_5$, $Fe(C_5H_5)_2$ and $Ti(i\text{-}OC_3H_7)_4$ was investigated during partial evaporation of the spray of different precursor solutions. Two solvents, ethanol and o-xylene, with different thermal stabilities are used to prepare solutions of these precursors. The spray is formed by the standardized spray nozzle of a SpraySyn burner and heated in a quartz plug flow reactor up to 800 °C to provide the energy required to initiate the simultaneous evaporation and decomposition of the spray. Decomposition products are analyzed by ToF mass-spectrometry with micro probe sampling. The relevance of the low temperature conditions for the spray flame process is substantiated by measurements of the spatial temperature distribution of the SpraySyn flame. Depending on the relative thermal stability of the precursor and the solvent, the less stable component can initiate decomposition of the more stable component, resulting in different reaction patterns of the four solutions.

Kinetics of partial oxidation of methane/additive mixtures for polygeneration processes: High-pressure shock-tubes experiments

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Higher-value chemicals can be produced from methane with small exergy losses by partial oxidation if the chemical conversion proceeds in internal combustion engines (ICE). This can be used in the context of polygeneration processes counteracting the fluctuation in renewable power sources. By varying the fuel/air ratio the engine can be operated from pure electric power generation to pure energy storage. Intermediate operating conditions are partial oxidation at moderate and very fuel-rich conditions. Under these conditions, additives ere needed to increase the reactivity of methane for stable ICE operation already at low preheating temperatures. Kinetics models, which are necessary for simulations to develop and optimize the polygeneration process, are not sufficiently validated for the fuel-rich and high-pressure conditions relevant for these processes. Therefore, ignition delay times of fuel-rich methane/(additive)/air mixtures were measured in a shock tube at about 30 bar and temperatures between 600 to 1650 K. Dimethylether, dimethoxymethane, *n*-heptane and diethylether were used as additives. At $\phi = 2$, measured ignition delay times agree well with simulations using different mechanisms from literature. Synthesis gas (CO, H_2) is the main product at $\phi = 2$. The influence of the various additives is quite similar. For the production of higher hydrocarbons, the equivalence ratio must be increased. Very fuel-rich mixtures ($\phi = 10$) were used because the temperature increase during the reaction of these mixtures is quite low (< 450 K), so that post-ignition temperatures stay below the lower temperature limit of soot formation. The predictions of some of the literature mechanisms show again a good agreement with the experiments. As a further parameter to improve and validate the mechanisms at $\phi = 10$, product compositions were determined by gas sampling in the cooling phase with a fast-opening valve and subsequent GC/MS analysis. Besides H_2 and H_2O, CO and higher hydrocarbons like C_2H_2, C_2H_4, C_2H_6, and C_6H_6 were detected as main products. About half of the carbon of the methane consumed is converted to CO, the other half forms higher hydrocarbons. Only a small part of the mechanisms, which contain a sufficient benzene and PAH chemistry, can predict well the measured product composition.

Spatiotemporal Coherent Anti-Stokes Raman Spectroscopy in the Recirculation Zone of Bluff-Body Stabilized Premixed Methane/Air Flames

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Laser diagnostics play an important role in the work of advancing clean combustion technology for future aircraft propulsion systems, internal combustion engines and gas-turbines. This optical tool has the ability to perform non-intrusive measurements in-situ, and providing scalar information with excellent spatial and temporal resolution. Among a wealth of techniques, coherent anti-Stokes Raman scattering (CARS) spectroscopy is established with a capability to look deep into the molecular structure and acquire reliable temperature and species concentration from gas-phase reactive and non-reactive media [1]. We are developing spatiotemporal CARS spectroscopy for a capability to probe dynamical thermochemical processes, e.g. targeting low turbulence phenomena encountered in recirculation zones of combustors. In these recirculation zones, a mixing occurs between the fresh reactants and the products which can act as a flame stabilizing mechanism, and it is through the shaping of these recirculation zones much of the emissions (NOx, particulates, CO and unburned hydrocarbons) can be reduced. To achieve simultaneous spatially- and temporally correlated data obtained with CARS, a laser system has been built which producing a synchronized output of high-peak power femtosecond- and picosecond laser pulses generated at 1 kHz repetition rate. The system consists of three main modules which are all fitted on the same table. In this way, disturbances due to vibrations of the platform are minimized, which allows for robust usage also at aero-propulsion facilities.

In this work, I will discuss benefits of spatiotemporal CARS diagnostics and show initial results from a measurement in the recirculation zone of a bluff-body stabilized premixed methane/air flame.

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Modelling urea deposit formation and decomposition on SCR catalysts

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Selective Catalytic Reduction (SCR) with urea-water-solution (UWS) is a widely applied technique in automotive applications for removal of nitrogen oxides (NO_x). To meet future emission legislation, it is preferred to move the catalysts further upstream, closer to the engine, to achieve higher temperatures and thus higher NO_x conversion. Therefore, the mixing section is reduced. Injected UWS droplets can reach the catalyst inlet and form film and deposits in the catalyst which can block the channels. The formation and decomposition of urea deposits have been studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mass spectroscopy (MS) of pure deposit components and mixtures with catalytic material.

A multiphase tank reactor model (DETCHEM^{MPTR}) from Tischer et al. [1] is extended by methods to calculate the reactions on the interface to the catalytic surface. For this, the interaction with liquid phases (UWS film, melting of deposits, condensation of gas species), solid phases (urea deposits), the gas phase (especially isocyanic acid hydrolysis and a $NH_3/NO_x/SCR$ mechanism [2]), gas diffusion through liquid film, transport limitations in the catalyst, storage effects and catalyst ageing is taken into account.

The interaction of UWS with the catalytic surface was implemented into the DETCHEM^{MPTR} code and the model was calibrated for the beginning of urea decomposition by adding new reactions occurring on the catalytic surface. These results were compared with experimental data from TGA, DSC and MS.

Deposit interaction with catalytic material is a promising way for deposit removal or even for prevention of deposit formation. In addition, gas phase interaction with the catalytic surface, in particular isocyanic acid hydrolysis and subsequent ammonia formation, is enhanced, resulting in better NO_x conversion at the inlet of the catalyst.

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Investigation of solid fuel particle group combustion using volumetric OH-LIF imaging and diffuse backlight-illumination

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The transition from single to group coal particle combustion is experimentally investigated in a laminar flow reactor using state-of-the-art laser diagnostics. Simultaneous volumetric OH-LIF imaging using a novel laser scanning technique is combined with time-resolved diffuse backlight-illumination (DBI) providing fundamental insights into flame topologies. In our previous work, the OH-LIF measurements have been applied to study the single coal particle combustion [1] and revealed a higher accuracy for the ignition delay time detection compared to the broadband luminosity imaging technique [2]. In this study, three-dimensional visualizations of volatile flames are first demonstrated on single particle combustion and then applied to characterize the flame topology associated with group particle combustion. The particle number density (PND) determined by instantaneous DBI images covers a wide range from the individual particle combustion to group combustion enabling the determination of transitional effects. While an enclosed volatile flame is observed with dominant spherical structures at low PND, enveloping flames surrounding non-flammable regions reveal distinct features as PND increases. The corresponding physical process is described by exploring the effect of local gas temperatures. The particle velocity affected by the inter-particle and particle-gas interaction is analyzed along the axial and radial direction. The ignition delay time increases gradually as PND increases. The non-flammable region is quantified by evaluating the non-flammable volume ratio R_{nf}. The non-flammability becomes pronounced if PND exceeds a limit of approximately 0.37 mm^{-3}, which corresponds to an inter-particle distance of $4d_p$ in this study. The results suggest similar effects of lower gas temperatures and the appearances of non-flammable regions with decreasing inter-particle distance, which were also observed in various numerical investigation [3-4]. The experiments provide a novel dataset for the validation of numerical modelling and contribute a better understanding of the group combustion of pulverized coal particles.

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The role of renewable fuels in low-carbon societies

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What will be the future of combustion when the use of fossil fuels becomes marginal? Answering this question starts by dissociating combustion of fossil fuels. In low-carbon societies, *renewable fuels* can be synthesized based on renewable energies while combustion keeps on playing a major role (e.g. combined heat and power, wood gasification ...). Indeed, a mobility based on fuels or a long-term storage based on molecules could become the most interesting options. To decipher the problem and understand the role of synthetic fuels in low-carbon societies, we use EnergyScope TD [1], a model for regional energy system which represents with the same level of detail the heating, mobility, and electricity sectors. The model optimizes the design of the system and its operation while minimizing its annual yearly cost.
By forcing the energy system to emit less greenhouse gases, the model selects the best mix of technologies to manage the growing share of renewable energies. Through its application to two different countries (Belgium [2] and Switzerland [3]), the model brings out the renewable fuels as a competitive option for renewables integration, energy sectors decarbonisation and long-term storage In the case of a low-carbon Belgium, renewable fuels represent 68 TWh, which is equivalent to 18% of the total primary energy. These renewable fuels are used for power supply (22%), heating (16%), freight mobility (33%) and passenger mobility (29%).

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Flame synthesis of carbon metal-oxide nanocomposites in a counterflow burner

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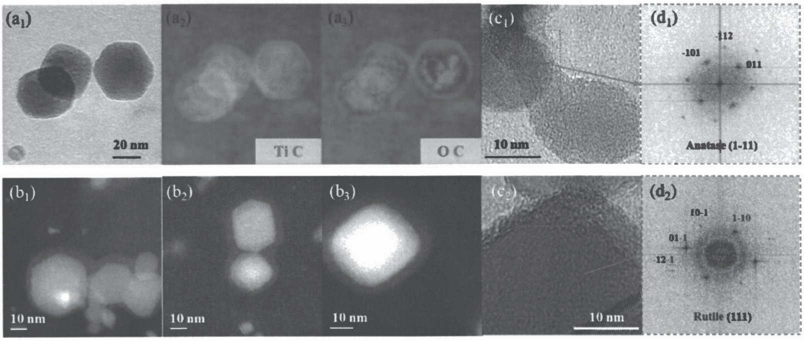
Core-shell carbon metal-oxide nanocomposites are synthesized in a well-defined counterflow burner. Benefitting from the two-nozzle configuration, the nanocomposite morphology can be controlled by adjusting the precursor loading rate and fuel mass fraction independently. In-situ laser diagnostic method and transmission electron microscopy (TEM) technique are used to investigate the formation mechanism of nanocomposites. In the presence of a 532 nm laser pulse, laser-induced incandescence, Ti atomic emissions, and C2 swan spectra that appear simultaneously can indicate the particle volume fraction, titanium component, and carbon component, respectively. By increasing the precursor loading rates, both the measured laser diagnostic signals and the TEM images demonstrate that the titania component rises proportionally with the precursor concentration while the carbonaceous layer thickness remains unchanged. As further revealed by the axial profiles of the three signals, the formation and growth of the nanocomposites is composed of two steps. The first step is the reaction, nucleation, collision, and coagulation of metal oxides in the oxidizer side of the flame sheet. The second step is the formation of carbonaceous layers surrounding the metal oxides, which can be regarded as the heterogeneous nucleation of the carbonaceous species in the fuel-rich zone. By adjusting the precursor concentration and the fuel mass fraction, we can achieve independent control of the first and the second steps, respectively, thereby actively tailoring the core size of metal oxides and the carbonaceous layer thickness.



Experimental assessment of the release of Nitrogen, Sulfur and Chlorine species during pyrolysis of coal and biomass in CO_2 atmosphere

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In oxyfuel combustion, the substitution of nitrogen in the combustion atmosphere by recycled flue gas containing high concentrations of carbon dioxide is accompanied by a considerable change in the combustion behaviour of the solid fuel. The release of minority species, such as sulphur, nitrogen and chlorine compounds from the fuel plays an essential role in the design process of oxyfuel power plants, since significant corrosion and emission issues arise from these species.

In this study, the release of nitrogen, sulfur and chlorine species during pyrolysis of US-American bituminous coal with high sulphur content and a torrefied biomass was studied in an entrained flow reactor. With the entrained flow reactor, particle heating rates comparable to those observed in a full-scale furnace can be achieved. Pyrolysis experiments were performed at different reactor temperatures in carbon dioxide atmosphere. Gas samples were extracted from the reactor and analysed for their NO, N_2O, NH_3, HCN, H_2S, SO_2, COS and HCl content using mass spectrometry and FTIR spectroscopy.

The results showed that the formation and release of the measured minority species changes with temperature and differs between the two fuels considered in this study. It was found that the N_2O concentration decreases rapidly with increasing temperature, while the NO concentration increases. The release of NH_3 increased with increasing temperature, whereas the release of HCN decreased. Compared to the bituminous coal, more N_2O and NH_3 and less HCN was released during pyrolysis of the torrefied biomass. Moreover, the concentrations of SO_2, COS and HCl were higher during pyrolysis of the U2 coal.

Experimental and modeling study on the auto-ignition properties of ammonia/methane mixtures at elevated pressures

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The present worldwide concern about global warming has stimulated the development of carbon neutral energy technologies to mitigate the need of fossil fuels and the emission of greenhouse gases. In this sense, ammonia (NH_3) is regarded as one of the most viable alternatives to produce carbon-free energy, presenting high energy density and ease of storage and handling. However, its low flammability and high NO_x emission potential inhibit the implementation of pure NH_3 in these systems [1]. Methane on the other hand is a favorable low emission fuel and can be used as a co-firing fuel in ammonia combustion to promote the reactivity and control the emission levels [2,3]. However, knowledge of the ignition properties of NH_3/CH_4 mixtures at intermediate temperatures and elevated pressures is still scarce.

This study reports ignition delay times of $NH_3/CH_4/O_2$ mixtures diluted in Ar or Ar/N_2 over a temperature range of 900-1100 K, pressures of 20 and 40 bar, and equivalence ratios of 0.5, 1.0, and 2.0. The results demonstrate that a higher CH_4 mole fraction in the fuel mixture increases its reactivity, and that the reactivity decreases with increasing the fuel-oxygen equivalence ratio. Most recent mechanisms of Glarborg et al. [4] and Li et al. [5] were compared against the experimental data for validation purpose. Both mechanisms can predict the measurements fairly well. Detailed modeling for emissions indicated that adding CH_4 to the fuel mixture increases the emission of CO and NO_x. Moreover, addition of CH_4 complicates the reaction pathway of both CH_4 and NH_3 consumptions due to the cross reaction between carbon and nitrogen radicals.

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Numerical simulation and experimental research of biomass and coal coupled combustion

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Coal and natural gas remain the important fuel for the present and future in China. Recently, biomass has attracted researchers' attention for its superior higher heating value (HHV) and low-emission features. It is a tendency of utilization of coupling combustion of biomass and coal (or natural gas) which will help to reduce the consumption of fossil fuels [1]. Sometimes we mix biofuel with coal to achieve better control of the burning process [2]. In this research, we firstly focus on the gasification gases of the mixture of coal and biomass according to different mixture ratio. The pyrolysis and gasification gases of coal, biomass, and their mixture mainly include hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2) and water vapor steam (H_2O). Different composition may cause different combustion performance. We compare different gases in order to find the best mixture ratio. Secondly we will analyze the combustion behaviors of the particle mixture of biomass and coal by TG-FTIR (Thermogravimetric Fourier Transform Infrared spectroscopy). The simulation of the mixture gasification gas of biomass and coal is in progress using CHEM1D. The in-house laminar code CHEM1D [3] was used for modeling a one-dimensional free flame for the determination of the flame temperatures, laminar burning velocity and flame thickness. The experiment method was Heat Flux Method (HFM) which is an accurate alternative for measuring laminar burning velocity of a number of fuels at atmospheric pressure [4], sub and super pressure.

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Pyrolytic reactions of methyl formate: Shock-tube studies and kinetic modeling

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Due to the limited availability of fossil fuels and their impact on climate change, so-called e-fuels produced from sustainable electric energy sources attract more and more attention in current research. In this context, the combustion chemistry of the ester group, which is a structural feature of various biodiesel components, is gaining importance [1]. Since methyl formate is the smallest organic species bearing an ester group, it can serve as a prototypical compound to study the general role of ester groups in combustion processes. It is obvious that from the high-temperature kinetics of methyl formate, information about the kinetics of higher esters can be inferred, and insofar the combustion mechanism of methyl formate can be considered as a link between those of C_1-hydrocarbon fuels and higher organic esters.

In our poster contribution, we present and discuss shock-tube experiments on pyrolytic reactions of methyl formate. Two different shock tubes with two different detection techniques were used namely hydrogen atom resonance absorption spectrometry and time-of-flight mass spectrometry. This combination allows observing a variety of species in a time-resolved manner. The obtained experimental concentration-time profiles are modeled on the basis of a reaction mechanism from the literature [2]. Rate coefficients of selected elementary chemical steps in this mechanism are adjusted by also taking into account results from quantum chemical and statistical rate theory calculations. The major aspects of these mechanistic modifications as well as the kinetic characterization of the elementary steps will be discussed.

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On the “anhysteretic state” of MILD combustion process

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MILD combustion [1, 2] processes occur with mixtures highly diluted and pre-heated by a strong recirculation of hot exhausted gases (thus mass and sensible enthalpy) within the combustion chamber. This strategy configures a homogeneous process based on continuous auto-ignition of mixtures with composition outside or close to flammability limits. MILD combustion processes present unique physical/chemical features, drastically different from traditional combustion systems, that should be discussed at basic levels for the fine comprehension of the process itself.

Within the palette of sub-processes ascribable to MILD combustion regimes, this work focuses on “Homogeneous Backmixing Ignition” processes. Such a term identifies a combustion process that evolves in a system in which inlet fresh reactants and outlet combustion products are mixed in homogeneous conditions.

The reference elemental reactor is a CSTR (continuously stirred tank reactor) [3].

In the present study the influence of several parameters on the stability of Backmixing Ignition process has been evaluated for CH_4-O_2-N_2 in a CSTR, moving from traditional air condition to diluted ones. The methane-air system is characterized by a S-shaped curve (hysteresis) with respect to the mixture preheating temperature (T_{in}), with a weakly- and strongly-burning steady state branches and an unstable steady state branch. The S-shaped curves are characterized with respect to mixture residence time (τ). As τ decreases, the hysteresis behavior moves to higher temperatures decreasing its extension with respect to T_{in}, up to reach an “anhysteretic state”. Such a behavior is further analyzed for different levels of mixture dilution. As the dilution level of the mixture increases, the “anhysteretic state” moves towards lower T_{in} and higher τ, corresponding to longer chemical characteristic times. This behaviour suggests that MILD combustion systems are less prone to instabilities.

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Polygeneration by partial oxidation of fuel-rich Methane/air mixtures in an HCCI engine – Different approaches to achieve auto-ignition

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Polygeneration is the combined production of work, heat, and chemical product output in a single reactor. In this work an internal combustion engine was used as a reactor for the partial oxidation of methane. This process is examined theoretically and experimentally. The experiments were performed in a single-cylinder engine with 332 cc. displacement, originally designed for liquid-fuel octane-number measurements. The engine was modified to reach compression ratios of up to 20 and to run on gaseous fuels with continuous intake-manifold injection by mass-flow controllers. The engine was fueled with stochiometric and rich CH4/air mixtures at equivalence ratios from 1.0 to 2.4. Both spark ignition (SI) and, for very rich mixtures, homogeneous charge compression ignition (HCCI) were investigated. In addition to the crank-angle resolved in-cylinder pressure, the chemical product output was speciated with a commercial exhaust-gas analyzer. Methane with its low reactivity is not an appropriate fuel for HCCI with lower compression ratios. Thus, different combinations of intake heating, the addition of reactive additives (DME and ozone) and compression ratio variation where investigated. Additionally, simulations from a single zone model where conducted to investigate the effect of ozone on auto-ignition kinetically.

Operation in SI mode resulted in increasing misfires for equivalence ratios higher than 1.5. In HCCI mode operation was stable for equivalence ratios from 1.2 to 2.4. Operation with around 10 mol% DME as additive was possible at 150°C intake temperature for a compression ratio of 10. Increasing the compression ratio reduced the amount of DME needed for stable operation significantly. Even operation without additive and preheating was possible at compression ratios of 18 and 19. It was found that small amounts of ozone substitute major part of the DME additive. The strong effect of ozone could be contributed to early OH radical and methyl hydroperoxide formation during the compression stroke.

Energy transition combustion research & challenges: Eindhoven activities

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This contribution covers the global approach of the combustion group of Eindhoven University of Technology towards what we see as relevant research required for the energy transition ingredients with a focus on combustion applications that covers the 4 sections headed by the present authors. In condensed form they contain different potentially green fuels consisting of hydrogen, ammonia, fuels for heavy internal combustion engines and metals. The embedding in our current set of research approaches, like the Flamelet Generated Manifolds method, HFM, and Heat Flux Method, HFM, is included in an implicit way. It also includes its crude research challenges but is omitting the specific details. About details, together with our general focus and vision we are open for discussions and suggestions.

Transition metal borides as electrocatalysts: State of the art and first investigations of the activity of iridium boride

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The water splitting reaction is an important reaction to produce hydrogen by solar devices as a storage possibility and source of green energy. To enable this reaction under low applied voltages electrocatalysts are used. To enhance the properties of catalysts for oxygen evolution reaction (OER) as well as for hydrogen evolution reaction (HER), it is important to understand electrocatalytic mechanisms. [1,2]
Recently, there has been great interest in transition metal borides as electrocatalysts due to their high stability. Thus, it is necessary to study the electrocatalytic activity of various compounds and examine which changes in structure and composition lead to a higher or lower activity. We have tested different binary and ternary transition metal borides for OER. Most of them showed a lack in activity and how difficult it is to find new catalysts for OER. Nevertheless, first measurements have shown that iridium borides have a suitable electrocatalytic activity which is obvious because iridium oxide is a benchmarking catalyst [1,2], but the activity of iridium borides has not been reported to date. Iridium borides crystallize in similar compositions but with different structures. Herein we compare the activity for OER as well as HER of two iridium borides with a different structure.

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Transient thermal boundary layer development and flame wall interaction studies using 1d HRCARS and TGP in a constant volume chamber

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Unburned hydrocarbon emissions (UHC) are an important contributor to greenhouse gas emissions. Near-wall transient heat transfer and flame-wall interaction (FWI) are topics of great importance in understanding emissions in downsized internal combustion (IC) engine and gas turbine technology. This talk describes simultaneous measurements using 1D hybrid fs/ps rotational CARS (HRCARS), thermographic phosphors (TGP) and CH* imaging performed in an optically-accessible constant volume chamber designed to study transient near-wall heat transfer processes and FWI. HRCARS provides single-shot gas-phase temperatures, while thermographic phosphors measures wall temperature and CH* provides insight regarding the flame front position. The simultaneous measurements are used to resolve thermal boundary layer (TBL) development and the associated gaseous heat loss for three important processes occurring in IC engines: (1) an unburned-gas polytropic compression process, (2) FWI, and (3) post-flame, gas expansion, and cooling processes. During an unburned-gas mild polytropic compression process, measurements show a small wall heat flux (≤ 5 kW/m^2) that yields to an appreciable temperature stratification through a developing TBL, with adiabatic compression in the core gas and polytropic compression near the wall. During FWI, gases closest to the wall ($y < 0.2$mm) continue to experience thermal loading from polytropic compression until the flame is within ~1.4 mm from the wall. Immediately afterwards, the wall first senses the flame as wall temperatures begin to increase. The thermal profiles support the understanding of an unburned thin layer of fuel close to the wall. During FWI, gas temperatures up to 1150 K impinge on the wall, producing peak wall heat fluxes (620 kW/m^2) and prompting an increase in wall temperature ($\Delta T = 14$ K). Gaseous heat loss in the post-flame gas occurs rapidly at the wall, yielding a TBL of colder gases extending from the wall as wall heat flux slowly decreases.

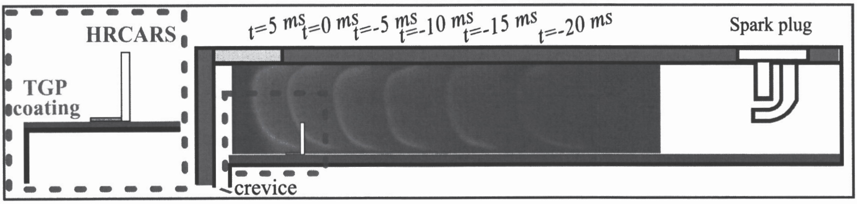

Figure 1. *Experimental setup for the combined 1D-HRCARS, TGP AND CH*.*

Kinetics study of dimethoxymethane in shock tube: Experiment and modeling

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Oxygenated hydrocarbons like oxymethylene ethers (OMEs) are gaining importance as neat alternative fuels ("biofuels") and as blending agents in gasoline and Diesel fuels. Kinetics data of DMM oxidation are scarce. For the development of reaction mechanisms, experimental data are needed. In particular, the initial reaction channels are important. In this context, shock-tube experiments have been performed to investigate the thermal decomposition and oxidation of the oxygenated hydrocarbon dimethoxymethane (DMM; $CH_3OCH_2OCH_3$) in a shock tube. As primary initial reaction channels of DMM decomposition, two bond-fission pathways are considered: $CH_3OCH_2OCH_3 \rightarrow CH_3O + CH_2OCH_3$ (1) and $CH_3OCH_2OCH_3 \rightarrow CH_3 + OCH_2OCH_3$ (2). For studying the thermal decomposition of DMM behind reflected shock waves, three detection techniques were combined: (i) H-ARAS (atomic resonance absorption spectrometry) for time-resolved observing the formation of H atoms (ii) HRR-TOF-MS (high-repetition-rate time-of-flight mass spectrometry) for the measurement of the depletion of DMM, (iii) GC/MS (gas chromatography coupled with mass spectrometry in a single-pulse shock-tube) for determining the composition of stable reaction products. The experiments span a temperature range of 1100–1430 K, a pressure range of 1.2–2.5 bar and initial reactant mole fractions from 0.5 ppm (for H-ARAS experiments) to up to 10,000 ppm (for HRR-TOF-MS experiments). The rate overall constant was obtained and follows the Arrhenius expression $k_{\mathrm{total}}(T) = 10^{13.28\pm0.27} \exp(-247.90\pm6.36\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{s^{-1}}$ with 30–40% uncertainty. By implementing k_{total} in a recently published DMM chemical kinetics combustion mechanism [1], it was also possible to successfully reproduce the measured product composition. Additionally, ignition delay times of DMM were measured in a high-pressure shock tube at 30 bar and $\phi = 0.5$, 1, and 2.

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A novel approach to methanol production: integration of solar hydrogen, Chemical Looping Combustion and syngas production via Reverse Water Gas Shift reaction

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Syngas is widely used as an intermediate in the chemical industry. Syngas production method strongly affects its composition, namely the H_2/CO ratio, which is assessed as a benchmark of efficiency for its further application (i.e. methanol)[1]. Currently, syngas is produced either by gasification of biomass/solid fuels or by methane reforming (steam- or dry-). An alternative way to produce syngas is using the CO_2 emitted by power plants. Through the Reverse Water Gas Shift reaction (RWGS), CO_2 can react with a H_2 stream, yielding H_2O and CO[2]. The availability of a pure H_2 stream could be a limitation for the practical applicability. The most effective way to tackle this problem could be to produce H_2 by means of water electrolysis, using electricity from renewable sources. In addition, by flanking the RWGS reaction with the Chemical Looping Combustion (CLC), as innovative technique for CO_2 capture, it is possible to encourage the use of captured CO_2 as a starting reagent for syngas production *via* RWGS reaction.

In this work, an innovative process layout for methanol production by syngas is investigated. The proposed layout promotes the integration of chemical storage of renewable energy *via* H_2 production by water electrolysis, CO_2 utilization and syngas production *via* RWGS reaction. In detail, the process consists in a CLC unit, which provides CO_2 to the RWGS reactor, an electrolysis unit, which supplies hydrogen to the RWGS reaction and enriches the syngas produced, in order to ensure an adequate composition for the production of methanol. RWGS products are separated from water by condensation, which is recycled to the electrolysis unit. Finally, the syngas is injected into the methanol synthesis unit.

Further developments of this work aim to determine optimal operating conditions and carry out an analysis of costs, in order to investigate the feasibility of industrial implementation of alternative processes for methanol production.

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Experimental investigation of ethanol/diesel dual-fuel combustion in a heavy-duty diesel engine

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Ethanol is a promising alternative fuel applicable in the internal combustion engine by virtue of its sustainability and soot-reducing potential. In this study, ethanol is injected into the intake port while diesel is directly injected into the cylinder of a heavy-duty commercial diesel engine enabling dual-fuel operation. The main goals of the study are to probe the ethanol substitution ratio and load range and assess the resulting engine performance and emissions. Tests were performed with the original calibration at several loads using the European Stationary Cycle. The results show that ethanol mass ratios of up to 80% may be reached at low to medium loads without misfire. Addition of ethanol can reduce soot emissions, with no consistent effects on NOx emissions. As the ethanol mass ratio increases, dual-fuel operation suffers from incomplete combustion progressively. Increased HC and CO emissions are, however, believed to be manageable by a diesel oxidation catalyst at high loads. Both combustion and thermal efficiency decrease at low load when ethanol is introduced. However, thermal efficiency at medium load increases from 49.1% to 50%. For medium to high loads, thermal efficiency first increases to 50.7% and 49.7%, respectively, then decreases due to sub-optimal combustion phasing at high ethanol mass ratios. It is noteworthy that the pressure rise rate, ringing intensity and peak pressure may appear to limit the ethanol ratio to below 40% for medium to high loads. However, this can be mitigated by delaying diesel injection timing, phasing the combustion later, without a large efficiency compromise.

Mass spectrometric study of iron- and silicon-containing hydroxides and oxides in particle forming flames

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Iron oxide, and silica nanoparticles are produced in flame reactors for a variety of applications in medical technology and pharmaceutical industry. The synthesis in a flame reactor is particularly attractive since it produces high-purity nanoparticles at scalable production rates in a continuous gas-phase synthesis process, but the fundamental chemical interactions during this process are poorly understood. These can be investigated in laminar, low-pressure flames stabilized on model burners with mass spectrometry as analytical technique.

Species profiles of intermediates formed in hydrogen/oxygen/argon flames doped with tetramethylsilane and iron pentacarbonyl have been measured. These reveal that for both precursors, hydroxides, e.g. $Si(OH)_4$ and $Fe(OH)_3$, are dominant intermediates in the gas phase. In addition, oxides can be detected. The relative concentrations of the intermediates can be manipulated by the choice of flame conditions. Consequently, particle formation pathways can be influenced, if the reaction patterns are rationalized in a reaction mechanism.

Morphology, composition and optical properties of flame-made nanoparticles

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Climate change has been identified as "one of the greatest challenges of our time" [1]. New policies must be implemented to limit the temperature increase below the 1.5 or 2 °C above pre-industrial levels following the recent Paris Climate Agreement. Most importantly, new technologies for the removal of long-lived CO_2 emissions from the atmosphere need to be developed and scaled-up to attain the above limits by 2050. Unlike CO_2 emissions that have an atmospheric lifetime of more than 1000 years, soot is a short-lived atmospheric pollutant with a lifetime of about 7 days. So, reducing soot emissions could have an immediate impact on global warming, delay climate effects induced by CO_2 and "buy" significant time for implementation of new technologies for reduced CO_2 emissions. In this regard, quantifying the impact of soot morphology and composition on its optical properties is essential for monitoring of soot emissions from different combustion sources and the accurate estimation of the climate impact of soot.

Here, this understanding is advanced by discrete element modeling (DEM) of soot surface growth, aggregation [2], agglomeration [3] and oxidation [4] along with rigorous comparison to experimental data at various combustion conditions from different laboratories. The DEM-derived agglomerates are coupled with the discrete dipole approximation (DDA) to account for soot morphology and composition revealing the evolution of its light absorption [5] and scattering [6] during combustion in premixed flames. This DEM-DDA algorithm can be readily used for advancing soot optical diagnostics, as well as for a more accurate estimation of the climate impact of soot.

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Reducing Emissions of Industrial Furnaces: Two Case Studies in the Port of Rotterdam

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We study the non-premixed turbulent combustion of natural gas at factories in the harbor of Rotterdam. Our first and second industrial partner produce cement and anodes for aluminum production, respectively. The reduction of thermal nitric-oxides and of carbon-monoxide is a primary concern for both partners. Experience has shown that the required fundamental understanding of the pollutant formation processes cannot be gained empirically. Numerical simulation is therefore expected to play an ever increasing role in reducing the environmental footprint of the material production industry.

Previous simulations of the cement kiln allowed to completely eliminate unscheduled plant shutdowns[1]. Research is currently focussed on the optimization of geometry of the secondary air inlet channel [2]. The design in operation causes zones with locally high heat release. Our objective is to remove these zones by an even secondary air inflow. We encounter the challenge of ensuring a sufficient heat transfer from the flame to the material bed.

Current research on the anode baking furnaces aims toward building a simulation model that is able to guide the interpretation of the measured emissions [3]. As in the case of the cement kiln, the model with consist of a Favre-averaged description of the flow, a species description of the combustion, a discrete ordinate description of the radiative heat transfer and a conjugate heat model for the insulating lining. Both the use of the OpenFoam and of Comsol Myultiphysics software is currently being considered. In the future the model complexity will have to be increases to be able to access the variability of the gaseous fuel composition. The mixing of natural gas with hydrogen is a likely option to be consider.

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Identification of combustion regimes for highly diluted NH3/O2/N2 mixtures in a Jet Stirred Flow Reactor

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The implementation of a hydrogen-based economy is incompatible with inexpensive and safe transport infrastructures [1]. The use of chemical fuels as hydrogen carrier has been attracting the attention of scientific and industrial communities because they offer higher volumetric density than pure hydrogen.

Among these alternative fuels, the interest in ammonia has grown in several fields, such as gas-turbines, naval and automotive transportation engines. Ammonia is a carbon-free molecule, thus in compliance with CO_2 reduction emission policies, it is easy to transport with an already available delivery network and consolidated production technologies [2]. However, NH_3 physical and chemical properties, i.e. flame velocity, low calorific value, minimum ignition temperature and the potential high NOx emissions in combustion processes could represent a limit for the application of ammonia as alternative fuel. Due to its properties, the oxidation of ammonia requires the implementation of non-conventional combustion technologies, such as low temperature combustion under diluted conditions [3]. Thus, an analysis of combustion regimes is mandatory, because such operative conditions may implicate the occurrence of thermal-kinetic instabilities, due to the coupling between low-temperature oxidation chemistry and heat exchange phenomena.

In this framework, the aim of the work is to present an experimental characterization of NH_3 oxidation in a Jet Stirred Flow Reactor as a function of mixture inlet temperature and composition. Several combustion regimes are identified, such as slow combustion, dynamic behaviors and high temperature combustion. The shift from the identified regimes occur at noticeable temperatures and the transitional mode from a regime to another one is affected by the inlet mixture composition. Numerical simulations were realized in order to identify the controlling reactions. Even if the ammonia oxidation chemistry is not completely understood, to some extent, the considered kinetic models are able to predict the different kinetic regimes and describe their dependence on system temperature and mixture composition.

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Numerical approaches for analysis, reduction and validation of detailed chemical mechanisms of new generation fuels

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The ongoing conversion of energy systems to fuels from renewable sources poses significant theoretical and technological challenges. In-depth knowledge of the behavior of the combustion phenomena arising from the adoption of alternative fuels is required but the increasing complexity of these phenomena due to the variability of the combustion conditions (including unsteady) and of the fuel composition (implying flexibility) limits the application of already established methods.

This contribution focus on the need to develop new and more computationally efficient methods for the analysis of combustion phenomena requiring very detailed chemical mechanisms. An integrated numerical approach, including the analysis of the behavior of complex chemical mechanisms with the bifurcation theory, and the skeletal reduction of chemical mechanisms, a-priori or the on-the-fly within CFD codes, is at an early stage of development.

The continuation algorithm allows for an effective study of the behavior of the system over wide ranges of the parameters, helping to identify critical conditions (ignition and extinctions) or the occurrence of unsteady equilibrium solutions ("combustion instabilities") [1]. Fast and automatic skeletal reduction is valuable to perform CFD simulations of combustion systems where chemistry plays a significant role. The entropy production analysis demonstrated to be an effective tool for this task [2]. The two methods are not independent: the regions where critical conditions arise are often those more difficult to reproduce with reduced mechanisms. Thus, their knowledge allows for a better validation of reduced mechanisms and for the increase of the predictive capabilities of the simulations [3]. Examples of applications showing the performances of these methods will be presented.

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Spectral modeling of an oxy-fuel pulverized coal fired boiler considering non-gray gas and particles

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Thermal radiation through gases and particles matter is the dominant mode of heat transfer in pulverized fuel fired boilers. Radiation influences ignition, flame temperatures and consequently the formation of soot. Due to the combustion of pulverized biomass or coal with recycled flue gas and pure oxygen, the amounts of carbon dioxide and water vapor in the flue gas of the power plant boiler are increased in comparison to the air-fired process. Both molecules show strong absorption and emission characteristics in the infrared wavenumber region providing enhanced thermal heat radiation on the evaporator tubes along the furnace walls. To precisely predict the thermal radiation, the non-gray behavior of gas and particle radiation has to be accounted for.

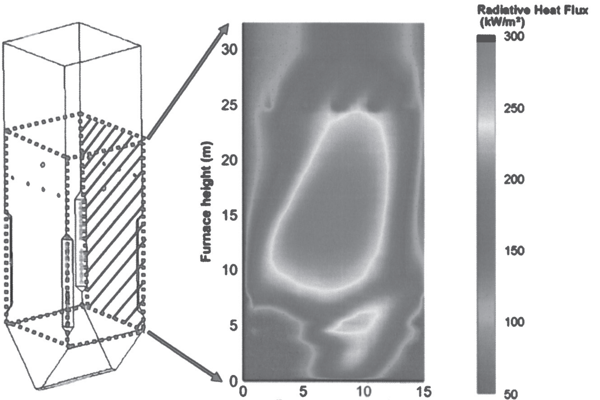

Figure 1: Radiative heat flux at the sidewall of an industrial furnace. Radiative heat flux calculated with NBCKM and Henyey-Greenstein (HG) phase function for particle scattering.

In this study, results from a CFD simulation of a 250 MW_{el} and 15 x 15 x 90 m dimensioned coal fired industrial boiler are used as boundary conditions for a radiation simulation. This simulation is based on temperature, species, pressure and particle distribution from the CFD simulation. The radiation heat flux is calculated with a Narrow Band Correlated-k Model (NBCKM). To consider non-gray particles, different scattering phase functions are evaluated. A study of the mesh size from 31,250 up to 250,000 cells shows a slight difference in the calculated radiative heat flux.

Cerium Phosphates as potential luminescent oxygen sensing materials at elevated temperatures

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Combustion engines driven by regenerative fuels remain a promising and important technology to solve current problems of energy storage in the automobile sector. A detailed understanding of the combustion process is essential for the development of novel efficient engines, and it is achieved by analyzing gas flow, temperature und atmosphere by thermographic methods. These are widely used for analyzing the gas phase by a combined application of thermometry and particle image velocimetry with laser spectroscopy [1]. This technique provides spatial resolution of the temperature distribution, but little is known about its potential for simultaneous gas sensing. Former investigations indicated that the luminescence of some phosphors does in fact depend also on the oxygen partial pressure [2, 3]. This effect is considered to be undesirable for thermometry. However, it might provide information about the atmosphere that could be useful for a better understanding of combustion processes.

$CePO_4$:Tb shows bright green emission and is mentioned in literature as a potential oxygen sensor because of its reversible redox-sensitive luminescence [4]. With these promising properties for the application as an oxygen sensing phosphor it is mandatory to evaluate the behavior at elevated temperatures, which was so far not reported. For that reason, we investigated luminescence properties of phosphors at temperatures up to 200 °C in O_2/N_2 atmosphere. The nanosized $Ce_{0.85}Tb_{0.15}PO_4$ shows good oxygen sensitivity but also high temperature quenching at 200 °C. Cerium is responsible for the redox quenching and was therefore partially replaced by lanthanum. $Ce_{0.4}La_{0.4}Tb_{0.2}PO_4$ shows a high oxygen sensitivity and furthermore a high intensity at elevated temperatures. These properties are promising for the application as luminescent oxygen sensor at elevated temperatures [1].

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Machine learning-based analysis of the early flame kernel in a spark-ignition engine to predict combustion performance

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The understanding of the sources of cycle-to-cycle variations (CCVs) in spark-ignition (SI) engines is critical in optimizing engine performance and reducing pollution. Variations of in-cylinder motion are regarded as important sources of engine CCVs and are unavoidable due to the nature of turbulent flows. However, through a better understanding of the processes involved in the interaction between engine flows and early flame CCVs, significant improvements in engine efficiency can be realized.

Engine performance in an optically accessible single-cylinder SI engine is investigated by means of machine learning (ML) analysis of planar Mie scatter images of the early flame (7.2 crank angle degrees after ignition) and the cycle maximum pressure (P_{max}). After a binary classification of cycles with high (HC) and low (LC) P_{max} based on a median threshold of 34.6 bar, the dataset of 615 cycles is carefully evaluated to select 32 flame features as input parameters for the ML analyses. Different decision tree (DT) -based supervised ML methods are used to test the accuracy of the prediction of cycles with HC or LC. In order to train and test all ML methods, a nested cross-validation (CV) technique along with a grid search with 10-fold CV on each inner-fold is used. This technique outputs the mean and standard deviation of the outer models' accuracies as well as the mean feature importance. In addition, the feature space is reduced by selecting a subset by hand and by using the first 10 principal components of a principal component analysis.

All ML methods yielded a prediction accuracy of at least one standard deviation above chance level ($p_{\text{chance}} = 50\%$), with the most accurate being the logistic regression model and hand-selected subset (65%). The probability of the burned gas occurring to the left of and below the spark plug is much greater in HC cycles than in LC cycles. This initial analysis is confirmed by the CV feature importances, which show that two features, the value of the x-coordinate of the leftmost and bottommost positions, are by far the most significant in predicting cycles of HC. Machine learning models were then tested with the logistic regression method with these two features only. This standalone model yielded a prediction accuracy of about 60% which means that even with such limited information as the leftmost and bottommost position of the 2D cross-section of the early flame at one point in time, CCVs can reasonably be predicted. Using such a reduced standalone model, more complex features such as flow velocities and spark energies can be implemented in the future to gain further insight into the underlying mechanisms behind engine CCV.