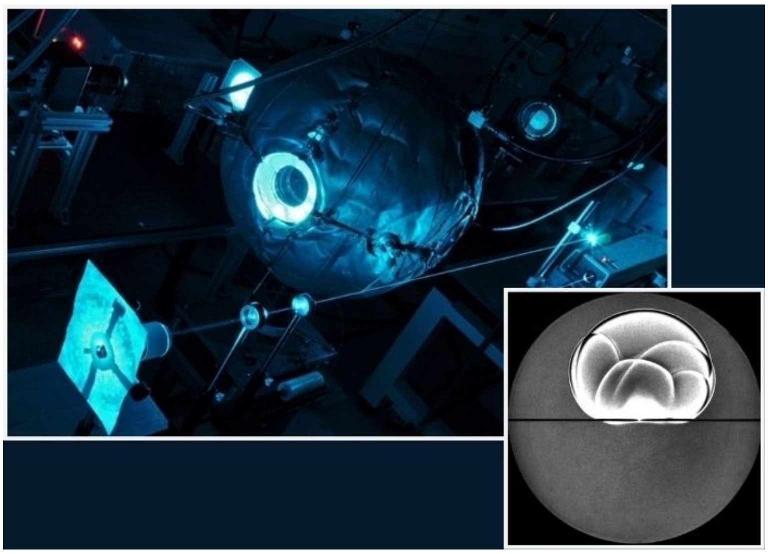
7th International Flame Chemistry Workshop



Combustion Institute 40th International Symposium
Emphasizing Energy Transition

July 20th-21st 2024
Politecnico di Milano, Milan, Italy

Book of Abstracts

Summary

Introduction

Increasing concerns of energy security, climate change and the challenges of the carbon-neutral energy transition drive the design of alternative fuels and their implementation in advanced combustion devices.

The understanding of fundamental aspects of high and low temperature combustion such as ignition, flame chemistry and emissions of new fuels (H_2, NH_3, sustainable aviation fuels, etc.) or under new and advanced combustion conditions (high pressure, plasma assisted, flameless, supercritical combustion, etc.) supports the design of new technologies while expanding technical and scientific knowledge in a key energy sector.

The *International Flame Chemistry Workshop* gathers scientists and researchers from a wide variety of areas such as chemistry, physics, physical and theoretical chemistry, mechanical, aerospace and chemical engineering to discuss and foster collaboration over many fundamental challenges.

Theoretical, modelling and experimental aspects will be discussed in relation to five topics:

1. Sustainable fuels combustion (LFS, IDT, pollutants): H_2, NH_3, SAFs
2. Advanced diagnostics for combustion measurements
3. Plasma combustion: experiments and modelling
4. AI-TST-ME: automation, benchmarking and knowledge transfer
5. Chemical Kinetics Mechanisms: Progress in Accuracy and Details

This booklet collects abstracts for oral contributions in the five topical areas above as well as poster contributions.

Wishing you all a fruitful workshop and an enjoyable time in Milan.

Workshop Chairs
Matteo Pelucchi – Politecnico di Milano, Italy
Bin Yang – Tsinghua University, China

Organizing Committee
Brandon Rotavera - University of Georgia, USA
Feng Zhang - University of Science and Technology of China, China
Andrea Comandini - CNRS Orléans, France
Liming Cai - Tongji University, China
Carlo Cavallotti – Politecnico di Milano, Italy
Federica Bozza – MZ Events, Italy

Advisory Committee
Stephen Klippenstein – Argonne National Laboratory, USA
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Workshop agenda

*Day 1 - **Saturday 20th July***			
	Moderator	**8.00-8.30**	Registration (WS + CI 40th ISOC)
Opening	*Matteo Pelucchi*	**8.30-8.50**	Welcome, agenda, discussion mode
Topic 1: Sustainable fuels combustion (LFS, IDT, pollutants): H_2, NH_3, SAFs	*Liming Cai*	**8.50-9.15**	Keynote Presentation - *Kai Moshammer*
		9.15-9.45	Short Presentations
			Zhen-Yu Tian
			Sven Eckart
			Yuyang Li
			Rodger Cornell
		9.45-10.30	Open Discussion
		10.30-11.00	Coffee Break
Topic 2: Advanced diagnostics for combustion measurements	*Andrea Comandini*	**11.00-11.25**	Keynote Presentation - *Alison Ferris*
		11.25-11.55	Short Presentations
			Robert S. Tranter
			Olivier Herbinet
			Wenhao Yuan
			Remy Mevel
			Nabiha Chaumeix
		11.55-12.30	Open Discussion
		12.30-13.30	Lunch
Topic 3: Plasma combustion: experiments and modelling	*Bin Yang*	**13.30-13.55**	Keynote Presentation - *Ramses Snoeckx*
		13.55-14.25	Short Presentations
			Xingqian Mao
			Yong Tang
			Wenting Sun
			Quentin Malè
		14.25-15.05	Open Discussion
Topic 4	*Feng Zhang*	**15.05-15.30**	Keynote Presentation - *Luna Pratali Maffei*
		15.30-16.00	Coffee Break
Topic 4: AI-TST-ME: automation, benchmarking and knowledge transfer	*Feng Zhang*	**16.00-16.30**	Short Presentations
			Sarah Elliott
			Kai Leonhard
			Judit Zador
			Emilio Martinez-Nuñez
			Lili Ye
		16.30-17.10	Open Discussion
Wrap-up	*Matteo Pelucchi*	**17.15-18.00**	Summary from Day 1
Posters		**18.30-20.30**	Poster Session and Dinner

Day 2 - ***Sunday 21st July***			
	Moderator	**8.00-8.50**	Registration (WS + CI 40th ISOC)
Topic 5: Chemical Kinetics Mechanisms: Progress in accuracy and details.	*Brandon Rotavera*	**8.50-9.15**	Keynote Presentation - *Jeremy Bourgalais*
		9.15-9.45	Short Presentations
			Fabien Goulay
			Xuefei Xu
			Lenny Sheps
			Malte Döntgen
			Shijun Dong
		9.45-10.30	Open Discussion
		10.30-11.00	Coffee Break
Wrap-up	*Matteo Pelucchi* *Bin Yang* *Andrea Comandini* *Feng Zhang* *Brandon Rotavera* *Liming Cai*	**11.00-12.30**	Open discussion on tasks, objectives and actions towards the *8th International Flame Chemistry Workshop*
		12.30-13.30	Lunch

Topic 1. Sustainable fuels combustion (LFS, IDT, pollutants): H_2, NH_3, SAFs

Keynote presentation

Sustainable Fuels Combustion – A Present and Future Perspective

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Sustainable fuel combustion represents a critical area of research and development aimed at reducing environmental impact while meeting global energy demands. This field encompasses the utilization of renewable and low-carbon fuels such as hydrogen, ammonia or Sustainable Aviation Fuels (SAF). Key aspects include the optimization of combustion processes to maximize efficiency and minimize the emission of pollutants, particularly carbon dioxide (CO_2) and nitrogen oxides (NOx). Experimental studies are crucial for understanding the combustion characteristics of these fuels, including their ignition properties, flame stability, and emissions profiles. The extensive methods developed over decades from research on conventional combustion systems are now being adapted and enhanced for greater sustainability. Fuel design, combustion processes, emissions, and aftertreatment are being re-examined with fresh perspectives, leveraging advanced experimental, theoretical, and numerical tools.

The keynote will give an overview of recent achievements in fundamental research of sustainable fuel combustion and will highlight chemical aspects associated with sustainable fuels. It will give a perspective on the question: What progress are we making in researching new fuels through both innovative and conventional approaches?

Sustainable Aviation Fuels (SAF) play a pivotal role in reducing the carbon footprint of the aviation industry. Derived from renewable resources such as biomass, waste oils, and even algae, SAF can significantly lower greenhouse gas emissions compared to traditional jet fuels. Since SAFs origin from different sources and their production routes are different, their chemical compositions may differ in their molecular structure and the types of hydrocarbons present, and consequently in their reactivity. Experimental approaches like ignition-delay time measurements in rapid compression machines and shock tubes as well as laminar flame speed measurements are used for fuel reactivity studies [1, 2]. However, even if sustainable, SAFs still contain mid- to long-chain hydrocarbons leading to PAH and soot formation if burnt incompletely [3].

Hydrogen offers the potential for near-zero carbon emissions when produced using renewable energy (green hydrogen) and is therefore another key player in the transition to sustainable fuel combustion. As the most abundant element in the universe, hydrogen can be produced from a variety of resources, including natural gas, water, and biomass. Hydrogen combustion offers the advantage of producing only water as a byproduct, eliminating CO_2 emissions. In comparison to hydrocarbon fuels such as natural gas, gasoline, and diesel, utilizing hydrogen as a fuel can improve thermal efficiency while decreasing carbon emissions. However, challenges such as its high reactivity and the risk of NOx formation must be addressed. Besides these combustion properties that can be traced back to its chemistry, it should be considered that hydrogen requires robust storage and distribution infrastructure when using it as a sustainable fuel in technical applications.

Ammonia is considered a molecule that is a suitable chemical to serve as a hydrogen energy carrier due to its high volumetric hydrogen density. However, extracting hydrogen from ammonia requires a significant amount of energy, thus it is inefficient to use NH_3 as a hydrogen source for fuel. Alternatively, the direct utilization of ammonia as a fuel has gained increasing attention in recent years and has emerged as a promising candidate for sustainable fuel combustion, particularly in the context of shipping and heavy industry. As a carbon-free fuel, ammonia offers the potential to drastically cut CO_2 emissions. The combustion of ammonia, however, presents problems, such as the formation of nitrogen oxides (NOx) and its relatively low reactivity, i.e., a slow burning velocity and a high autoignition temperature (or long ignition delay time) compared to conventional fuels [4].

As the individual fuels (SAFs, H_2, NH_3) pose a variety of challenges, mixing with other fuels, i.e. hydrocarbons, alcohols etc. may provide potential solutions to these problems. This involves for example mixing with reactive compounds like hydrogen, methane, dimethyl ether (DME), methanol, ethanol diesel, or gasoline as additives [5, 6]. However, for ammonia, as the overall reactivity increases, the different fuel chemistries can interact and lead to other/new pollutants such as HCN.

Advanced combustion techniques, such as flameless/MILD (moderate or intense low-oxygen dilution) combustion [7] and plasma-assisted combustion [8, 9], are seen as promising methods to expand operational conditions and minimize pollutant emissions for sustainable fuels. Low- to intermediate-temperature oxidation is particularly significant for achieving higher efficiency and reduced pollution in practical combustion systems. Consequently, kinetic studies within this temperature range are a focus for various fuel types.

To tackle the problems of sustainable fuel combustion, a deeper understanding of the chemistry underlying the phenomena must be achieved. This can only be done by improving and revising kinetic models. Experimental speciation in the form of concentration profiles (time-dependent and/or temperature-dependent) are essential validation targets. Experiments that previously could only be used to determine global measurements, such as ignition delay times, must be coupled with analytical instruments that can detect species (lasers, mass spectrometers, GC, etc.). Due to changes in chemistry, such as the interactions between N-chemistry and C-chemistry, existing experiments must be adapted to the new challenges such as *in-situ* laser diagnostic methods for the quantitative detection of HCN or by combining spectroscopic methods with advanced high-resolution mass spectrometry for the detection of highly-oxygenated species [10, 11].

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Speaker Biography

Kai Moshammer heads the working group *Properties of Liquids* at the German National Metrology Institute (PTB). He studied chemistry at the Karlsruhe Institute of Technology (former University of Karlsruhe), Germany and obtained his diploma in 2009. He then joined the University of Bielefeld (Germany) where he finished his doctoral dissertation in 2013 (Title*: Mass spectrometric analysis of laminar flames as model systems for alternative combustion concepts*). From 2014 to 2016 he was a postdoctoral appointee at the Combustion Research Facility (CRF) at the Sandia National Laboratories, Livermore, USA. Dr. Moshammer is an expert in experimental combustion analysis which includes methods like Molecular Beam Mass Spectrometry and Laser Diagnostics He was among others involved in the realization of several complex design projects and worked in diverse international project teams related to different topics in the field of combustion.

Invited presentations

Experimental studies of RP-3 partially premixed jet flames

Bipro Gain[1,2], Samuel Daniel[1,2], Muhammad Bilal[1,2], Muhammad Yousuf[1,2], Zhen-Yu Tian[1,2,3,*]
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Soot nanoparticles formed during combustion display a variety of nanostructures, which are influenced by different combustion parameters such as flame stoichiometry and temperature. It is essential to understand the generation and behavior of soot in order to develop effective strategies for mitigating its negative impact on air quality and the global climate [1, 2]. The main components of RP-3 aviation kerosene have been identified as primarily consisting of 64.15% alkanes, 18.48% cycloalkanes, and 15.88% aromatics [3]. Therefore, it is of utmost importance to comprehend the complexities of RP-3 combustion under different fuel conditions, including lean-to-rich ratios, in order to unravel the intricate mechanisms that govern soot formation. This study aims to characterize the properties of RP-3 jet flames and explore the intricate relationship between temperature and carbon formation.

After measuring the flame length, a significant increase in proportion to the growth of the equivalence ratio was observed. The flame color undergoes a significant transformation, changing from pale blue under fuel-lean conditions to bright green at stoichiometric levels, and to brilliant yellow under fuel-rich conditions. Transmission Electron Microscopy (TEM) of the soot particles revealed a size distribution at various flame heights, as shown in Fig. 1, which displays TEM images of carbon agglomeration with an equivalence ratio (ϕ) of 5.0. The soot agglomeration consists of several spherical particles that exhibit chain, branched chain, and ring shapes. The soot morphology at different flame heights clearly indicates a correlation between the height of the flame and the acceleration of carbon agglomerate growth. Furthermore, an insightful observation is presented, wherein an increase in flame height results in a gradual reduction in the contribution of surface growth to the overall size of the soot particles.

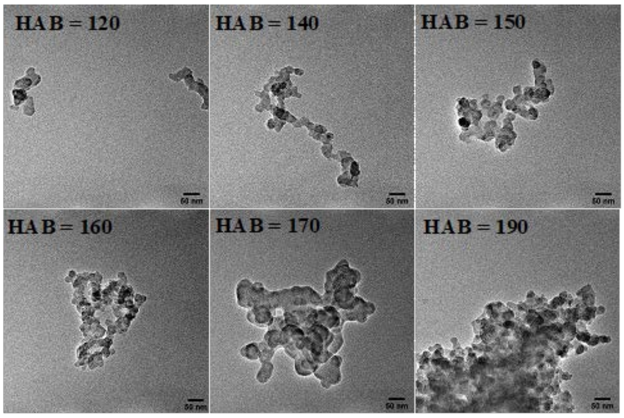

Figure 1. Microscopic morphology of soot agglomerate with different heights.

The analysis of soot particles obtained from RP-3 fuel combustion was conducted using Raman spectroscopy. This analysis provided important structural insights by examining the carbon D and G peaks shown in **Fig. 2**, which represent the primary Raman spectrum of newly formed carbon particles. The key features of this spectrum are the D (defect) and G (graphite) bands [4], with maximum values at approximately 1,350 cm^{-1} and 1,600 cm^{-1}, respectively. The presence of these two Raman peaks indicates the presence of amorphous or disordered carbon-based materials in general, suggesting that the soot nanoparticle had significant defects, particularly during its early stages of development [5].

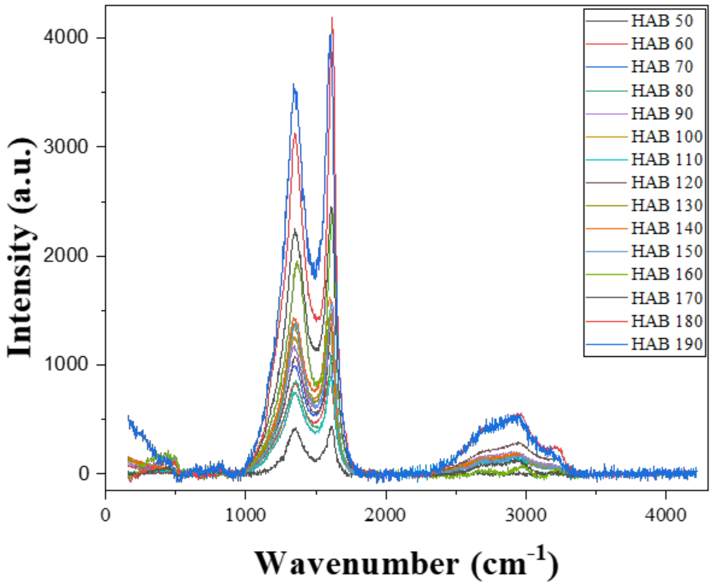

Figure 2. Raman spectroscopy carbon peak at varying vertical height above the burner (HAB) in flames.

In conclusion, the results of this study make a substantial contribution to the academic understanding of the intricate relationship between combustion conditions and the nanostructures of soot. The observed patterns in flame characteristics, along with the obtained insights into the morphology of soot, establish a solid basis for comprehending the fundamental mechanisms that govern the formation of soot in RP-3 flames. These findings enhance our understanding of combustion dynamics, offering valuable perspectives for the optimization of combustion processes and the elucidation of the environmental consequences associated with the production of soot by flames.

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Speaker Biography

Zhen-Yu Tian is a full professor at the Institute of Engineering Thermophysics, Chinese Academy of Sciences. His research interests include the development of advanced diagnostic instruments, combustion chemical reaction kinetics of key components such as aerospace/nitrogen-containing/SAF fuels, microgravity combustion, catalytic combustion, VOC removal technology, etc. He has published more than 200 papers, including more than 160 in SCI (including 52 CNF/PCI), 1 Springer Press textbook, 2 book chapters, and applied for/authorized more than 30 patents. He got several awards such as the National Outstanding Youth Fund, Humboldt Fellow, Beijing Outstanding Youth Fund, Sino-French Distinguished Youth Exchange Scholar of the Ministry of Science and Technology, Fellow of the Combustion Institute, Bernard Lewis Fellowship, Wu Zhonghua Outstanding Young Scholar, and IAAM Fellow, etc. Moreover, he serves as a member of several Award Committees and more than ten editorial members of international peer-reviewed journals.

Investigation into Hydrogen Integration within High-Temperature Oxyfuel Processes

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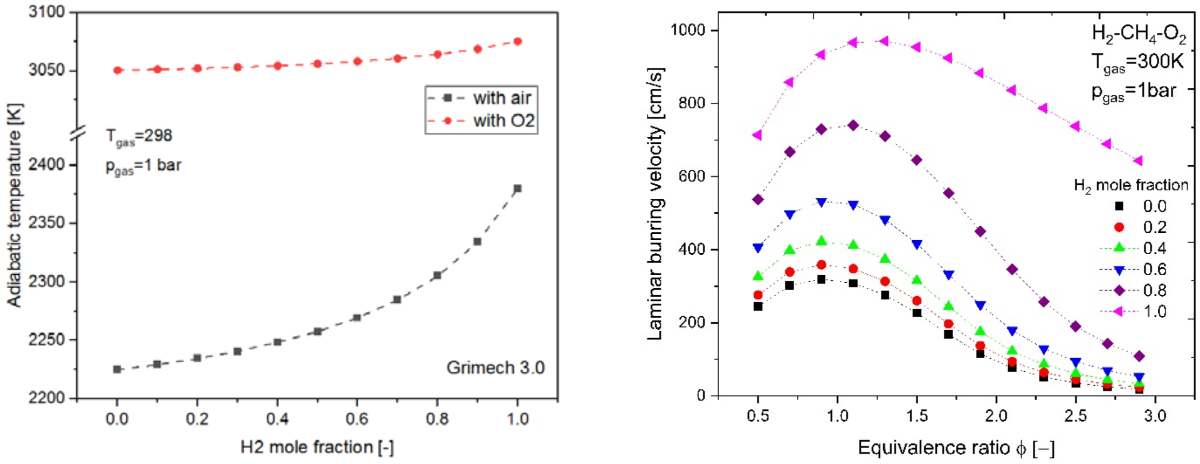
In high-temperature applications, conventional heating techniques might not transition entirely to electrification in the future, leading to an increased significance of alternative fuels. The transition from natural gas to hydrogen as a fuel source presents significant potential for shaping future energy strategies across diverse industrial domains. This study conducted an experimental investigation to assess the impact of incorporating hydrogen into natural gas flames during oxyfuel combustion processes.

Initially, a premixed oxy-fuel flame of hydrogen-methane blends was stabilized under atmospheric conditions. Subsequently, two distinct scenarios were investigated: low hydrogen admixture levels (ranging from 0 vol.-% to 35 vol.-%) and high hydrogen admixture levels (ranging from 50 vol.-% to 100 vol.-%) in the mixture. This experimental investigation employed a premixed burner operating at three different power levels. Flame characteristics were analyzed utilizing optical, spectroscopic, and thermal measurement techniques. The objective of this study is to assess alterations in flame morphology, temperature distributions at varying flame heights, and the formation of species within the combustion zone. To achieve this, an array of hydrogen-methane-oxygen mixtures at different equivalence ratios (ϕ = 0.8 - 1.2) was experimentally investigated.



A) B)

Figure 1. Calculated influence of hydrogen ratio A) on the adiabatic temperature and B) on the laminar burning velocity of a hydrogen/methane/oxygen mixture at P=1 bar varying the equivalence ratio [2].

Secondly a larger non-premixed natural gas-oxygen flame with varying degrees of hydrogen admixture, ranging from 0 to 100 vol.%, was investigated. The burner's power output ranged from 10 kW to 50 kW throughout the experimental trials. The oxyfuel burner underwent testing both as a free-flame and within a multi-segment combustion chamber [1]. A camera system was utilized to visually observe the combustion zone, capturing signals across visible (VIS) and ultraviolet (UV) wavelengths. Furthermore, radial and axial temperature profiles of the flame were recorded using type S thermocouples. The analysis was extended to the measurement of major exhaust gas components (CO_2, NO_x, O_2) across different fuel compositions and various equivalence ratios.

A) B)

Figure 2. A) picture of a 1.2 kW premixed natural gas/oxygen flame and B) 35 kW oxyfuel-flames from 0 to 100 vol.% hydrogen admixture

In the investigation of the, the primary objective was to assess the impact of hydrogen admixture on methane oxy-fuel combustion using a single-flame burner. Specifically, this study delved into the combustion characteristics across varying volumetric hydrogen concentrations in the fuel gas, different stoichiometries, and at three distinct burner power levels. These experiments revealed alterations in fundamental flame properties. Notably, an increase in temperature was observed with higher hydrogen content, necessitating adjustments in the process. Moreover, the flame exhibited a shortened length due to elevated burning velocity, accompanied by changes in emitted spectra. However, the influence of hydrogen admixture up to 35 vol.-% remained relatively minor, while significant property shifts were evident with hydrogen levels reaching 100 vol.-%, highlighting the challenge of stabilizing the flame under specific operational conditions. Geometrical adjustments or modifications to operating parameters were consequently necessary.

Regarding the larger-scale flame investigation, it was established that the burner could seamlessly transition from natural gas to hydrogen operation without structural alterations. Flame lengths experienced only marginal reductions across the entire hydrogen admixture range, while the flame root widened due to increased volume flow during hydrogen combustion. Significantly elevated concentrations of OH* radicals within the flame were observed. Temperature measurements indicated that flame temperatures were rising with increasing hydrogen content in the fuel gas, with only slight increases in temperature observed with radial distance. While these heightened flame temperatures could potentially offer advantages in production processes, the increased OH* concentrations might introduce complications in glass chemistry, necessitating process-oriented examinations.

Examination of exhaust gas components following water condensation revealed that in pure hydrogen-oxygen combustion, the exhaust gas primarily comprised oxygen. As the hydrogen content in the fuel gas rises, the NOx-levels also increase. The study also explored the influence of nitrogen content in the oxidizer, noting a sharp rise in NOx values with substantial hydrogen admixture and increasing nitrogen content in the oxidizer.

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Speaker Biography

Sven Eckart is a mechanical engineer with a strong background in combustion technology. From 2016 to 2019, Sven was awarded an ESF-PhD scholarship by the state of Saxony and the European Union. In February 2022, Sven successfully completed his Doctorate.
Since April 2022, Sven has assumed the role of Head of Group Combustion Technology and oversees a group of six PhD students, one Post-doc, and one exchange PhD student.
Sven is an active member of the DVGW (German Technical and Scientific Association for Gas and Water) and The Combustion Institute, German section. Sven is actively involved as PI in several ongoing fundamental research projects on laminar burning velocity and extinction processes as well as research projects for the introduction of green hydrogen into industrial processes in Germany.

Clean and efficient ammonia combustion for gas turbine applications: Are we close to the solution of this holy grail problem?

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Ammonia (NH_3) stands as one of the world's most important chemical products and serves as a novel carbon-free fuel and efficient hydrogen carrier. However, its practical implementation in combustion devices faces significant challenges due to the low reactivity and high pollutant emissions.

To address these challenges, we proposed strategies of fuel modification [1-7] and oxygen enrichment [8, 9] to enhance ammonia combustion and optimize fuel thermochemical properties for the purposes of gas turbine applications. Fuel modification strategies, including reactive fuel co-firing and ammonia pre-cracking, significantly enhanced combustion intensity for both laminar and swirl flames. A modified fictitious diluent gas method was proposed to separate the chemical and thermal effects [1]. The fuel modification strategies were found to be mainly controlled by the chemical effects, with thermal effects playing a minor role, leading to the trade-off between combustion enhancement and pollutant control. Consequently, achieving simultaneous combustion enhancement and pollutant control remains a "Holy Grail" challenge in ammonia energy conversion.

Oxygen enrichment provides an alternative strategy for enhancing ammonia combustion. For both ammonia laminar premixed flames and swirl flames enhanced by oxygen enrichment, we have observed remarkable simultaneous expansions in the stable combustion window to threefold and low NOx/NH_3 emission window to sixfold as the oxygen content increases from 21% to 40% [9] (Fig. 1). This phenomenon contradicts previous experiences in hydrocarbon combustion, where increased flame temperatures intensified NOx emissions predominantly due to thermal NOx formation. With advanced modeling analysis, this phenomenon can be attributed to an increase of about 400 K in adiabatic flame temperature originated from thermal effects, which facilitates the self-promoted pyrolysis of ammonia, thus promoting an overall increase in fuel pyrolysis rate and suppressing residual NH_3 emissions under fuel-rich conditions. This significantly widens the low NOx/NH_3 emission window and achieves simultaneous pollutant control during combustion enhancement. Furthermore, the staged combustion technique was integrated with oxygen enrichment, which was found to be effective in mitigating the significant NH_3-to-NO conversion penalty at the fuel-lean secondary combustion stage and eliminating residual hydrogen generated from the self-promoted ammonia pyrolysis [10]. Oxygen enrichment under axial staged regime reduces the optimized NOx emissions dramatically for ammonia swirl flames, with the optimized NOx emissions dropping to 72 ppmv by regulating the overall equivalence ratio.

In general, oxygen enrichment offers a promising clean and efficient combustion technology applicable to ammonia energy conversion in practical scenarios, which is specifically suitable for land-based gas turbines, boilers, and furnaces with available oxygen supply. However, achieving clean and efficient ammonia combustion still remains a long-term and elusive "Holy Grail" challenge under conditions where limited space hinders the additional supply of oxygen, such as in jet engines. In these scenarios, fuel modification strategies hold practical values for effectively enhancing ammonia combustion. The chemical insights gained from investigations on oxygen enrichment provide us with an important foundation for breaking the trade-off effect in fuel modification strategies, which will propel us toward the solution of the significant challenge in practical applications of ammonia combustion.

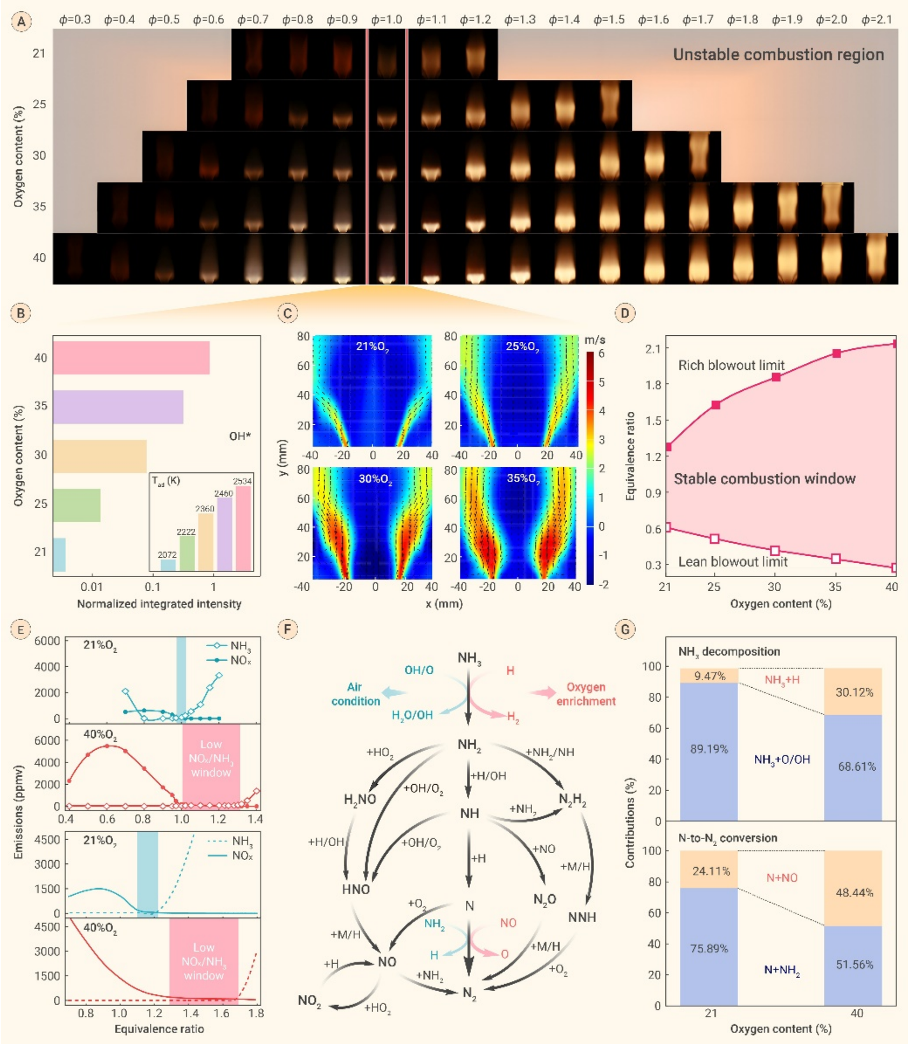

Figure 1. Experimental results and kinetic analysis of $NH_3/O_2/N_2$ flames. (A) Images. (B) OH* chemiluminescence and simulated T_{ad}. (C) Mean axial velocity distributions. (D) Lean and rich blowout limits. (E) NOx and NH_3 emissions measured in swirl flames (top) and simulated in freely propagating flames (bottom). (F) Main reaction network. (G) Contributions of key reactions to ammonia decomposition (top) and N-to-N_2 conversion (bottom).

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Speaker Biography

Yuyang Li obtained his PhD degree in 2010 and is now a professor and vice dean at School of Mechanical Engineering, Shanghai Jiao Tong University. His research interests include carbon-neutral energy and power, low-carbon combustion technologies for gas turbines and aircraft engiens, reaction kinetics and fluid dynamics in energy conversion, and novel combustion technologies. He has led over 20 projects and published over 180 papers, with over 5000 SCI citations and an H-index of 43. He was elected as a CI Fellow and has received the Research Excellence Award from the Combustion Institute, the China Youth Science and Technology Award, and the China State Natural Science Award (2nd Grade). He also has served as a colloquium coordinator of the 40th International Symposium on Combustion, the chair of Local Organization Committee of the 3rd Symposium on Ammonia Energy, a Section Editor-in-Chief of Applied Sciences, and a Section Editor of Journal of Ammonia Energy.

A Comprehensive H/N/O Ammonia Kinetics Model Informed by Diverse Experiments and State-of-the-Art Theory in an Uncertainty Quantified Framework

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Ammonia (NH_3) kinetics have received an extraordinary amount of attention in recent years due to NH_3's potential as a carbon-free fuel and energy vector. Additionally, NH_3 has other important applications that span a large scientific domain, including its pivotal role in managing NO_x pollution in industrial processes and its impact on energetic material reaction kinetics as an important intermediate species. As a result, the combustion community has generated substantial and diverse sets of NH_3 kinetics data in recent years that include species mole fraction measurements, experimental rate constant determinations, and high-level *ab initio* kinetics calculations. Considering the many thermodynamic states and chemical kinetic conditions emphasized by these far-reaching applications, there is an immediate need for comprehensive NH_3 kinetics models that maintain predictive capability over a wide range of temperatures, pressures, and reactant mole fractions. That said, there is no model currently available that remains predictive over such a wide range of conditions. To help address this shortcoming, the research presented here simultaneously considers comprehensive sets of uncertainty quantified (UQ) experimental data and high-level theoretical kinetics calculations using the MultiScale Informatics (MSI) approach. Preliminary results indicate that the resulting MSI NH_3 model exhibits improved predictions of numerous validation data sets that cover a wide spectrum of conditions – a clear indication that the model is exhibiting improved predictive behavior and should be considered for future ammonia research.

Introduction

To address persisting uncertainties present in NH_3 kinetics models, the research presented here simultaneously considered comprehensive sets of uncertainty quantified (UQ) experimental data and high-level theoretical kinetics calculations using the MultiScale Informatics (MSI) approach [1-3]. Most of the target data used to inform an *a priori* kinetics model focused on NH_3 oxidation by nitrogen-containing species as this chemistry is relatively uncertain and known to accentuate reactions important to many different kinetic systems (e.g., NH_2+NO_2 and NH_2+NO) [4,5]. The resulting MSI NH_3 model was tested against a wide spectrum of validation data purposely excluded from the MSI implementation to evaluate predictions at extrapolated conditions. All results presented here are preliminary as the MSI NH_3 model continues to evolve with the (almost daily) publication of new experiments and theory.

Preliminary Results

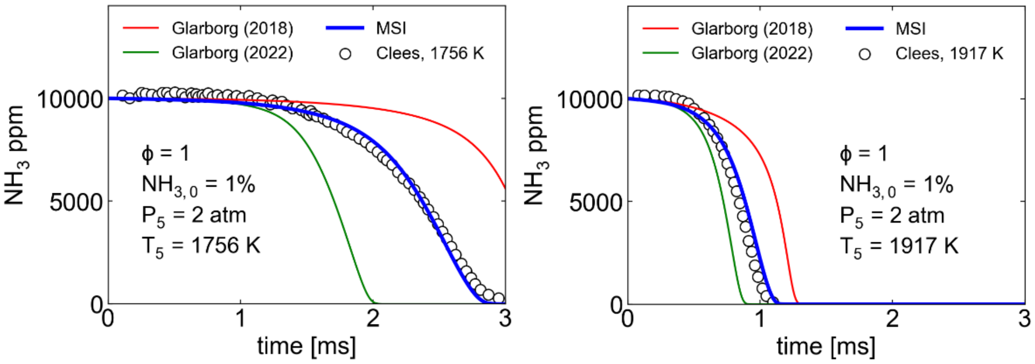

Figure 1. Shock tube measurements [6] vs. predictions from the preliminary MSI model (blue) and recent nitrogen chemistry models [7,8] (green and red). Note: this experimental data set was not included in the MSI implementation.

Predictions from the preliminary MSI model were compared to recent shock tube measurements [6] and other predictions from the nitrogen chemistry models of Glarborg et al [7,8] (which formed the foundation of the *a priori* model used for this MSI implementation). Figure 1 reveals that the preliminary MSI model offers substantially improved predictions when compared to both Glarborg et al. models.

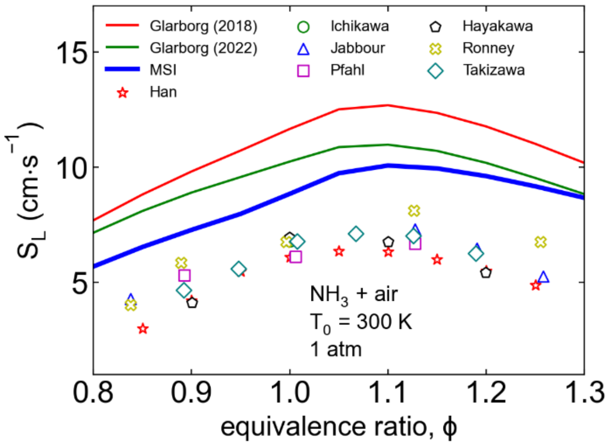

Figure 2. Flame speed measurements [9] vs. predictions from the preliminary MSI model (blue) and recent nitrogen chemistry models [7,8] (green and red). Note: this experimental data set was not included in the MSI implementation.

Predictions from the preliminary MSI model were compared to a compilation of NH_3/air laminar flame speed measurements [9] – a known shortcoming of many recent nitrogen chemistry models [7,8] that consistently overpredict NH_3 flame speeds. The preliminary MSI model provides significantly improved predictions that are likely in agreement with measurements when considering experimental uncertainties and the influence of third-body collision efficiencies [10]. Considering that no flame speed measurements were included in the MSI implementation, the results here indicate that the preliminary MSI model can successfully extrapolate predictions.

Preliminary Conclusions

An extensive target data set was used to constrain active parameters within an *a priori* multi-scale NH_3 model. The resulting (preliminary) MSI NH_3 model was able to accurately predict (nearly) all target data within estimated or reported uncertainties. Improved predictions of validation data sets purposely excluded from the MSI implementation suggest that the preliminary MSI model is capable of accurately extrapolating predictions. Once the MSI NH_3 kinetics model is finalized and published – which is expected to occur in the coming months – it should be considered for inclusion in many different kinetics models that either focus on NH_3 combustion or simply contain a NH_3 sub-mechanism.

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Speaker Biography

Dr. Rodger Cornell is a research engineer at the U.S. Army Research Laboratory. Over his 14-year career with the Army, Rodger has investigated the combustion, deflagration, and detonation of many different energetic materials and has assessed their performance in various Army-relevant systems. Rodger earned his PhD in mechanical engineering from Columbia University as a Department of Defense (DoD) Science, Mathematics, and Research for Transformation (SMART) Scholar. His dissertation focused on better understanding energetic material combustion through the combined use of multi-scale modeling and targeted chemical kinetic experiments. Rodger currently resides in Denver, Colorado where he is also a volunteer research staff member at the Colorado School of Mines under a recently established cooperative agreement with the Army.

Topic 2. Advanced diagnostics for combustion measurements

Keynote presentation

Recent developments in the use of optical diagnostics in shock tube kinetics experiments

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As carbon-free energy carriers and advanced propulsion strategies emerge as potential alternatives to the status quo, there is a rising need for high-fidelity experimental data to guide the development of models used to describe these new reacting systems. To better understand the underlying physics of these promising new fuels and processes, we find ourselves faced with new experimental challenges, some of which require new diagnostics and new or modified experimental facilities. Diagnostic techniques developed to study hydrocarbon fuels, for example, are often not sufficient to study nitrogen-based energy carriers.

Shock tube facilities paired with optical diagnostics have long been used to provide experimental measurements of species time-histories, ignition delay times, and reaction rates – measurements that have in turn informed the optimization of kinetic models. This keynote will highlight two recent shock tube studies as a means for sparking conversation about the current status of, and remaining needs for, optical diagnostics used to study reaction chemistry and flame phenomena in a shock tube. First, results from a recent shock tube multi-speciation study of ammonia oxidation will be presented [1]. Second, recent studies utilizing a shock tube to study flame propagation at high temperatures, with and without pre-ignition chemistry, will be highlighted [2,3].

Multi-species measurements in NH_3 oxidation experiments

As ammonia (NH_3) gains ground as a potential carbon-free energy carrier, there has been a commensurate increase in the number of kinetic models and experimental studies published to describe ammonia pyrolysis and oxidation. Nevertheless, recent works have highlighted wide discrepancies between kinetic model simulation results (e.g., [4]). Additionally, kinetic models that have been tuned to accurately predict experimentally measured global properties like ignition delay time or laminar flame speed often fail to capture time-resolved species trends, and vice versa. To address these observed discrepancies, shock tube experiments were conducted to simultaneously record ignition delay times and time-resolved species measurements [1]. A suite of UV and IR diagnostics was employed to target five time-resolved parameters in this work: NH_3, NO, excited amino radicals (NH_2*), excited hydroxyl radicals (OH*), and temperature.

Figure 1 shows representative time-history traces for NH_3, NO, and normalized NH_2* during stoichiometric NH_3/O_2 oxidation, dilute in argon (1% NH_3, 0.75% O_2, 0.5% CO_2, Ar), across a range of temperatures (1752-2445 K) at approximately 2 atm.

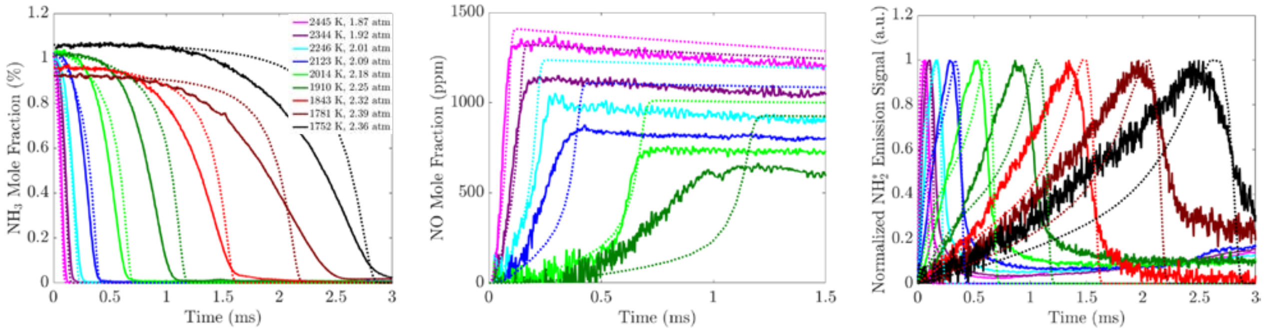

Figure 1. Time-resolve measurements of NH3, NO, and normalized NH2*, with comparison to simulated species time-hisories (0-D, constant-HP simulation using the mechanism of Glarborg et al. [5]). Plots adapted from [1].

The results of this study indicate persistent discrepancies between experimental and modeled results, and point to the pyrolysis reaction of NH_3+M=NH_2+H+M as a key reaction rate target for future experiments. The results additionally highlight the need for diagnostics capable of resolving short-lived radical species like NH_2.

High-temperature laminar flame speed measurements

The recently developed shock-tube laminar flame method has led to a new frontier in the use of shock tubes to study laminar flame behavior and propagation speeds at high temperatures. The shock-tube laminar flame approach, first introduced by Ferris et al. in 2019 [6], was developed as an alternative to conventional experimental laminar flame speed measurement approaches (e.g., the constant-volume, constant-pressure, stagnation flame, and diverging channel methods). While significant effort has been devoted to optimizing these conventional approaches and minimizing the uncertainty associated with measurements obtained using these techniques, they typically cannot be used to conduct flame speed measurements at unburned gas temperatures above ~700 K, due to the fact that at these high temperatures, the timescale for preheating the fuel/oxidizer mixture is on the order of, or longer than, the time for pyrolysis or autoignition. By using a reflected shock wave to preheat the fuel/oxidizer mixture, the shock-tube laminar flame technique successfully circumvents this problem, enabling flame speed measurements at previously unexplored high temperatures.
Figure 2 shows side-wall schlieren images from a representative shock-tube laminar flame experiment: passage of the reflected shock, flame initiation, and flame propagation. The shock-tube laminar flame method, paired with an optically accessible test section, has enabled the measurement of laminar flame speeds at unprecedented temperatures exceeding 1,000~K [2,7,8].

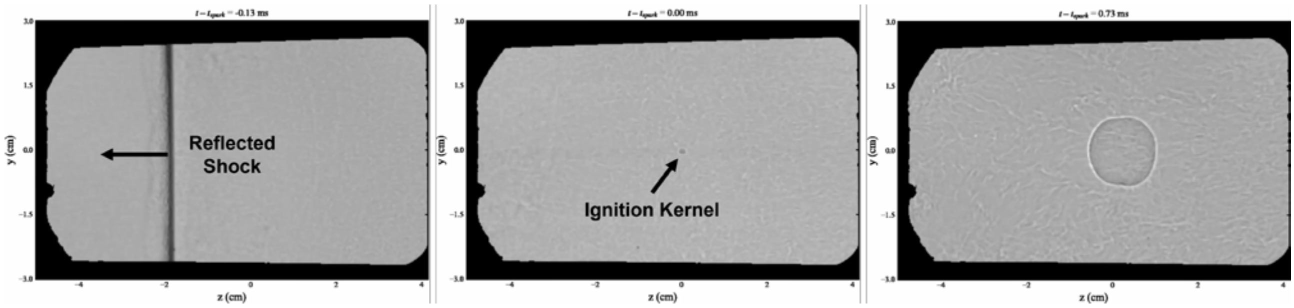

Figure 2. Side-wall schlieren images from a representative shock-tube laminar flame experiment (iso-octane in an oxidizer of 21% O_2/79% Ar, ϕ=0.9, 854 K, 1.0 atm).

Recent work, to be highlighted in this keynote, has focused on the study of application-relevant fuels (e.g., ethanol [2]) to better understand deficiencies in existing chemical kinetic models, and the study of complex flame phenomena (e.g., flame propagation accompanied by pre-ignition chemistry [3]). These results emphasize the importance of using low-uncertainty reaction rate measurements for small-molecule reactions and highlight the complexity of modeling flame propagation into reacting mixtures.

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Speaker Biography

Alison Ferris is an Assistant Professor in the Department of Mechanical and Aerospace Engineering at Princeton University. Prior to her current appointment, Alison held a joint appointment as a visiting Research Scientist at Technische Universität Darmstadt in the Institute of Reactive Flows and Diagnostics, and a post-doctoral scholar at Princeton University (2023-2024). From 2021-2023, Alison worked as a Research Scientist at Stanford University in Professor Ron Hanson's Shock Tube and Optical Diagnostics Laboratory. Alison's research interests include using shock waves and optical diagnostics to study the design, chemical synthesis, and reaction kinetics of sustainable fuels for use in current and next-generation energy and propulsion systems. Alison received her Ph.D. in Mechanical Engineering from Stanford in 2021, focusing on the development of a high-temperature laminar flame speed measurement technique and a combined gas chromatography-laser absorption diagnostic for time-resolved species measurements behind reflected shock waves. Alison received her M.S. in Mechanical Engineering from the University of Wisconsin-Madison in 2014.

Invited presentations

Investigating Chemical Kinetics with Synchrotrons and Shock Tubes

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Pyrolysis and combustion systems are inherently complex and obtaining kinetic and mechanistic data presents many challenges for experiment and theory. Even if the complexities of a flame environment are removed and one only considers chemistry, the problems remain daunting. The key chemical processes span large characteristic timescales and are strongly dependent upon concentrations, temperatures, and pressures. Generally, experiments are designed to either probe a key small reaction set in exquisite detail (e.g., unimolecular decomposition, radical + molecule, radical + radical etc.) or a global property that will constrain models (e.g., ignition delay, laminar flame speed etc.). No single type of experiment can provide the information needed to generate predictive models, rather combinations of methods are necessary along with theoretical chemistry. A particular challenge is to measure the time dependent concentrations of large numbers of open and closed shell species simultaneously and unambiguously identify the species and distinguish between isomers. For example, soot formation proceeds via the formation of polyaromatic hydrocarbons (PAH) which are built by reactions of smaller radicals and molecules. Considerable information exists on the formation of the one and two ring aromatics but as PAH grow the numbers of isomers rapidly increase as do the available reaction sites and mechanistic pathways hindering development of models. Pseudo steady state techniques, particularly when coupled with synchrotron-based photoionization methods, have been valuable in probing PAH formation. Key features of the synchrotron methods include simultaneous measurements of large numbers of radicals and molecules, often quantification of time-dependent concentrations, positive identification of species and some discrimination of isomers. However, it is difficult to generate the simultaneous high pressure and high temperature environments that are often of most interest in practical applications with these methods.

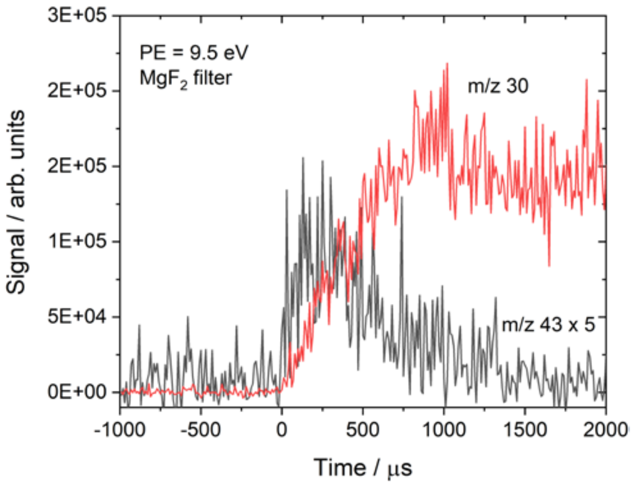

Figure 1. Signal/time profiles of n-propyl radicals (43) and H_2CO (30) from HRRST/TOF-MS experiments [1]. Due to the narrow, low photon energy there is no interference due to fragmentation products of species of the same m/z.

Shock tube techniques are well-suited to a very wide range of reaction conditions including high temperatures and pressures and form the backbone of experimental high temperature chemical kinetic studies. While it would be desirable to take advantage of synchrotron-based detection methods with shock tubes coupling the devices is a non-trivial problem. However, the problems have largely been overcome by developing a new class of miniature high repetition rate shock tubes (HRRST) [2-5]. These are being applied to elementary kinetics and global properties studies in the lab and at several synchrotron facilities. Here, the focus is on experiments performed at the Advanced Light Source (Lawrence Berkeley National Laboratory, USA) and Synchrotron SOLEIL (France). At both facilities an HRRST is coupled via molecular beam sampling to an ionization zone where energy selected photons from the synchrotron (typically 7-15 eV) create cations and photoelectrons. At the ALS the cations are analyzed by time-of flight mass spectrometry (TOF-MS) and at SOLEIL double imaging photoion photoelectron coincidence (i^{2}PEPICO) spectroscopy is used. Both instruments provide time-dependent concentration profiles and mass spectra and a method has been devised to account for rapid pressure changes during each shock [6]. From the ALS data mass resolved photoionization spectra (PIE) are also obtained which are useful for identifying limited numbers of isomers. Whereas the SOLEIL experiments yield mass-resolved photoelectron spectra (PES). These are considerably more information rich than the PIEs and can discriminate more isomers. The signal levels for both detectors are very low and it is necessary to signal average thousands of experiments at the ALS and tens of thousands of experiments at SOLEIL. Such averaging is only possible due to the unique features of HRRSTs.

In Fig. 1 an example of concentration histories from ALS studies on the reactions of alkyl radicals in the autoignition regime and ~10 bar is shown. These studies provided direct measurements of the disproportionation/recombination branching ratios at practical conditions that differ from the commonly used low T and P literature. The results also provide an anchor for theoretical predictions.

Figure 2 shows examples from PAH formation studies in the pyrolysis of toluene from work at SOLEIL. Mass spectra for radical and molecular species up to around m/z 360 (four to five aromatic rings) were resolved with S/N > 2. Within the spectra patterns were identified which were related to HACA processes involving C2 species, methylation reactions, C5 and C6 cycloadditions etc. These patterns are indicators of the types of active growth mechanisms and help to constrain the number of isomers that have to be considered in model development. For each m/z, PES were also obtained that contained information about the isomers contributing to the observed signal. In principle, PES can be used to identify the isomers and their relative contributions to the PES. However, reference PES for the individual isomers are needed and the literature is sparse, especially for multiring species. Consequently, a key part of the data analysis has involved collaboration with theoreticians to calculate PES for many species. With the literature and calculated PES and guidance from the MS patterns, it has been possible to estimate the isomer ratios for many PAH.

While HRRST/synchrotron techniques are reasonably mature the data analysis is still developing, especially for the i^{2}PEPICO method. One of the main issues is developing a large enough database of accurate PES for PAH to facilitate extracting isomer contributions from the experimental PES with confidence. Nonetheless, the studies provide considerable insight into PAH formation. An important question is ‘what level of detail is necessary to understand incipient particle formation? However, without sufficient knowledge of the mechanisms that can be operative in PAH growth it is difficult to produce reliable generalized models. The experiments discussed are beginning to provide considerable insight into PAH growth and may provide a basis for the development of generic, predictive models.

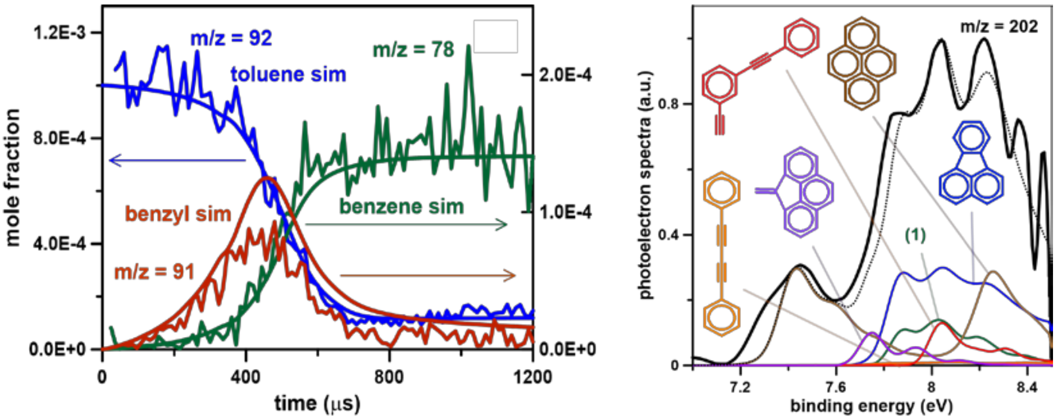

Figure 2. HRRST/i^{2}PEPICO experiments on the pyrolysis of toluene [6]. T=1362 K, P=6.6bar. Left concentration/time profiles corrected for pressure changes in ion source. Right: Isomeric contributions to the m/z 202 PES.

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Speaker Biography

Robert Tranter is a Senor Chemist in the Chemical Sciences and Engineering Division at Argonne National Laboratory. He obtained a BSc in Chemistry and a PhD in Combustion Chemistry from the University of Hull, UK. Tranter did a postdoc at the DLR, Stuttgart, Germany, which focused on the oxidation and recombination chemistry of the phenyl radicals. He then moved to the University of Illinois at Chicago where he held several positions working with John Kiefer and Kenneth Brezinsky on high temperature gas phase chemical kinetics with a variety of shock tube methods. Tranter’s research has explored the elementary chemical kinetics of species relevant to fuel efficiency, novel fuels, pollution reduction, particle synthesis and pyrolysis. He has developed and refined a number of experimental methods particularly with respect to shock tubes and the application of synchrotron-based diagnostics.

Progress in the dectection of intermediates formed during the oxidation of fuels

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The development of advanced technologies for the conversion of energy operating under unusual conditions (e.g., low-temperature oxidation, oxyfuel combustion) relies on a better understanding of the specific chemistry occurring during the combustion of fuels. At the same time, the shift from fossil fuels to renewable ones, namely those derived from biomass and those synthetized from hydrogen, introduces new types of molecules that differ from those present in conventional fuels by their structures (atom types other than carbon and hydrogen, functional groups…). This complicates the development of new technologies as their transformation implies new pathways which have been little studied to date.
A better understanding of the specific chemistry occurring during the combustion of fuels relies on the collection of experimental data and computational efforts to obtained data needed to build detailed kinetic models able to reproduce this chemistry. The collection of experimental data relies on the coupling of experimental devices, such as flow reactors operating under slow oxidation regime or burners, and various analytical tools with appropriate sampling method to probe species.
The jet-stirred reactor (JSR) is a type of continuous flow reactor that was used for gas phase studies of the oxidation of various fuels. This reactor is usually operated at steady state and the hydrodynamics relies on a perfect mixing of the gas phase. It was coupled to various analytical tools depending on the fuel under investigation and the type of species to probe. Most of the time it is necessary to use complementary techniques to detect a wide range of species as one technique is not able to detect all of them. A common technique found in many laboratories is gas chromatography which is powerful for the separation of stable species, but which has some limitations for specific species like hydroperoxides and radicals.
Cavity ring-down spectroscopy, a spectroscopic technique based on the absorption of infrared by species trapped in a cell and initially developed for atmospheric chemistry, was coupled to a JSR to detect hydrogen peroxide (Figure 1a), a degenerate branching agent participating to the reactivity of fuels at low-temperature [1,2]. The coupling between the JSR and the CRDS cell was achieved with a sonic probe to maintain the difference of pressure between the reactor and the cell and to freeze the reaction. But this sampling method did not allow the detection of radicals such as HO_2. This technique was also used during the oxidation of ammonia [3] to probe the fuel as it has strong absorption lines in the wavenumber range 6637–6643 cm^{-1}.

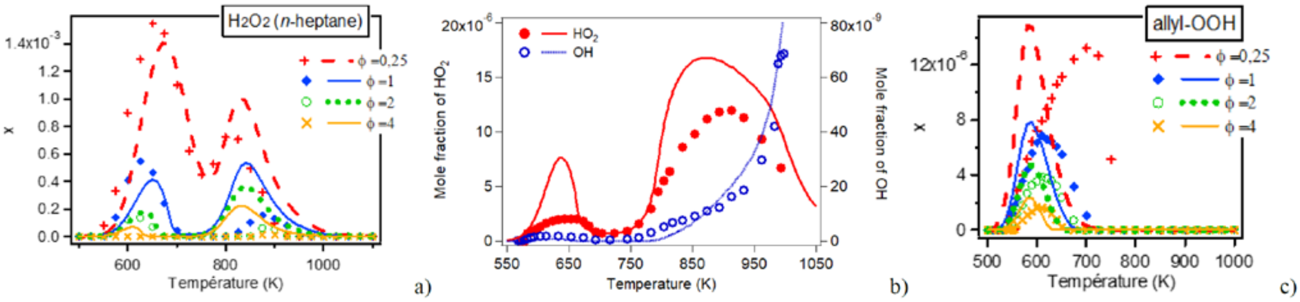

Figure 1. a) Quantification of H2O2 with CDRS in the oxidation of *n*-heptane [2]. b) Quantification of HO2 and OH by Fluorescence Assay by Gas Expansion [4]. c) Detection of allyl-hydroperoxyde with a SPI-TOF mass spectrometer in the oxidation of *n*-heptane [2].

HO_2 and OH radicals were detected [4] thanks an original coupling between a JSR and Fluorescence Assay by Gas Expansion (FAGE), another technique developed for atmospheric chemistry which is based on the fluorescence of the OH radicals. It also enables the detection of HO_2 radicals after conversion to OH by reaction with NO. The detection was achieved by admitting a sample of the exhaust gas from the JSR into the low-pressure cell through a nozzle. Figure 1b displays the HO_2 ad OH profiles recorded during the oxidation of *n*-butane. Mass spectrometry was used in different configurations according to the purpose of the detection. As a first example, a quadrupole mass spectrometer, with online sampling though a heated capillary tube, was used to probe the species in a JSR under rare conditions for which oscillations occur, enabling the visualization of species periodic evolution with time as displayed in Figure 2 [5].

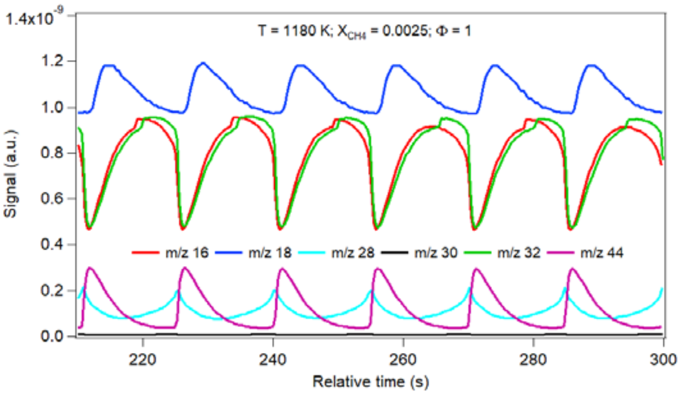

Figure 2. Species mole fraction evolution with time in a jet-stirred reactor operating under conditions for which kinetic oscillations occur during the oxidation of methane [5].

Mass spectrometry was also used to detect ketohydroperoxides, typical low-temperature branching agents, the sampling of which requires a great care due to their relatively low stability. The sampling was achieved with a molecular beam, and the detection was performed by a time-of-flight mass spectrometer with soft ionization by a tunable synchrotron vacuum ultraviolet radiation [6,7]. These studies highlighted the performance of the detection strategy for the detection of hydroperoxides, but they also shew that the identification of the different isomers, solely based on their photo-ionization thresholds, remains tricky. The measurement of photo-electron spectra can partially overcome this limitation as spectra are much more resolved as peaks reflect each electronic/vibronic state of the ion.

It was also demonstrated later that ketohydroperoxides could also be detected using a capillary tube for the sampling, but with precise temperature control of the transfer line to find an optimum to balance between condensation and destruction of the species [2]. This sampling technique was used in combination with a SPI-TOF mass spectrometer with high sensitivity and mass resolution enabling the detection a new class of species, namely alkenyl-hydroperoxides (Figure 1c).

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Speaker Biography

Olivier Herbinet received his engineering degree (2003) from the Ecole Nationale Sup´erieure des Industries Chimiques of Nancy, France and PhD degree (2006) from the INPL, Nancy, France (now University of Lorraine). His postgraduate research studies were made at the Lawrence Livermore National Laboratory (2007) in the Combustion Chemistry group. He joined the Combustion Chemistry group at the Laboratoire Réactions et Génie des Procédés, Nancy, France. His research interest is the study of the gas phase reactions (oxidation and pyrolysis), especially new modes of combustion (low-temperature oxidation, oxy-fuel combustion, ozone assisted oxidation) of fuel, biofuel and e-fuel transportation components. His activities in this area cover both combustion experiments at the laboratory scale (in particular the coupling of reactors with different diagnostics like gas chromatography, spectroscopic techniques and mass spectrometry) and the development of detailed kinetic models. He got his French habilitation degree in 2017. He teaches homogeneous combustion kinetics, heterogeneous catalysis kinetics and engineering, and analytical chemistry at the ENSIC of Nancy (chemical engineering department of the University of Lorraine) since 2007.

Combustion kinetic studies by flow reactor and photoionization mass spectrometry

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Flow reactor is a widely used laboratory reactor to investigate the combustion kinetics of fuels. In this presentation we will report our recent progress on the combustion kinetic studies by using photoionization mass spectrometry and two types of flow reactor.

Laminar flow reactor experiments

Laminar flow reactor has been utilized to investigate the high temperature pyrolysis of a series of aromatic hydrocarbons [1] in recent years. The flow reactor, with a length of 220 mm, was made of *α*-alumina to reduce wall catalytic effects. A small inner diameter (7 mm) was used to ensure strong radial diffusion effects and achieve adequately homogeneous reaction circumstance. During the experiment, intermediates, including radicals, isomers and polycyclic aromatic hydrocarbons (PAHs) were identified and quantified by using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). In our recent work on the combustion kinetics of aromatics, pyrolysis of *o*-xylene [2] and *p*-xylene [3] were investigated in the flow reactor at various pressures from 0.04 to 1 atm to explore the decomposition kinetics of fuel and evolution kinetics of PAHs. In the pyrolysis of *o*-xylene, key products related to fuel decomposition such as *o*-xylyl radical, *o*-xylylene, benzocyclobutene and styrene were detected (Figure 1) and provided new clues for the initial decomposition pathways of *o*-xylyl radical. C_9 PAHs (indenyl, indene and indane), phenanthrene and its methyl derivatives were observed as the abundantly produced bicyclic and tricyclic PAHs. The main formation pathways of bicyclic and tricyclic PAHs are found to be different at low and atmospheric pressures, depending on the major precursors produced. Particularly, the self-combination reactions of *o*-xylyl and the addition reaction of *o*-xylyl with benzyl and subsequent stepwise H-loss/cyclization reactions are found to be the main sources of methylphenanthrene and dimethylphenanthrene.

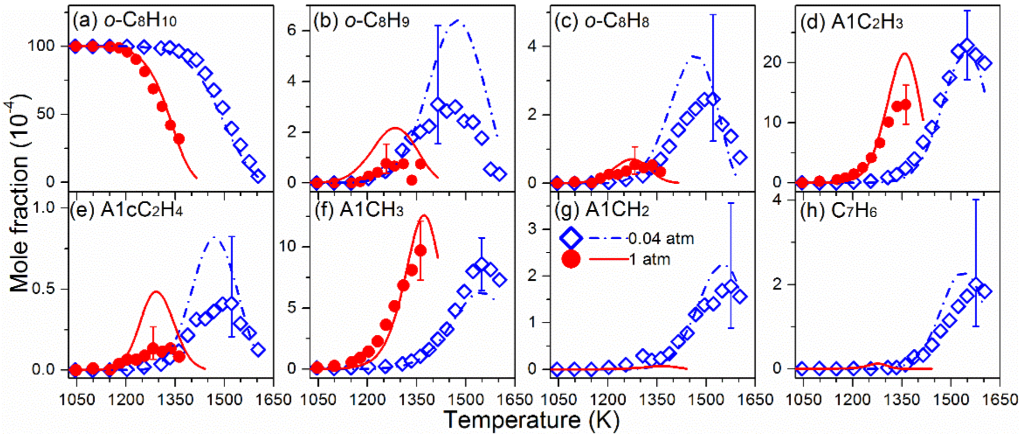

Figure 1. Experimental (symbols) and predicted (lines) mole fractions profiles of *o*-xylene (*o*-C_8H_{10}), *o*-xylyl (*o*-C_8H_9), *o*-xylylene (*o*-C_8H_8), styrene ($A1C_2H_3$), benzocyclobutene ($A1cC_2H_4$), toluene ($A1CH_3$), benzyl ($A1CH_2$) and fulvenallene (C_7H_6) measured in the pyrolysis of *o*-xylene in a laminar flow reactor at 0.04-1 atm [2].

To investigate the low- to high-temperature oxidation kinetics of fuels, an improved laminar flow reactor has been developed and combined with SVUV-PIMS. This reactor was specially designed to ensure a long constant-temperature heating region (400 mm). This setup has been used to investigate the oxidation of $CH_4/C_2H_4/NH_3/NO_x$, propene/NO_x and butene/NO_x mixture [4, 5]. Dozens of species were detected, including major products, hydrocarbon intermediates, carbonyl intermediates and nitrogenous intermediates. The isomers of carbonyl intermediates were separated unambiguously, *i.e.* acrolein and methylketene, acetaldehyde and ethenol. Some critical nitrogenous intermediates were also detected and identified in this work, including nitrous acid, nitromethane, 3-nitrosopropene and 3-nitropropene.

Micro flow reactor experiments

To probe the primary decomposition kinetics of fuels, a micro flow reactor was recently combined with SVUV-PIMS. The micro flow reactor (length: 40 mm, inner diameter: 1 mm) was made of SiC, and was heated by two electric heating wires. The coupling of micro flow reactor with SVUV-PIMS offers unprecedented advantages in exploring elementary reaction kinetics, superior to laminar flow reactors that feature significantly longer residence times. This approach enables the identification of primary intermediates and minimizes interference from secondary reactions, thus is highly beneficial for accurately elucidating the primary decomposition kinetics of fuels. By using this experimental setup, we investigated the decomposition kinetics of 1-indanone, which is a typical oxygenated PAH (OPAH) generated in the oxidation of aromatics [6]. The experiments were carried out at the pressure of ~0.08 atm and the residence time is around 60 μs. The experimental results revealed that styrene, phenylacetylene, and indenyl are major decomposition products of 1-indanone. A considerable amount of reactive radical intermediates including 1-indanonyl, benzyl, fulvenallenyl, phenyl and cyclopentadienyl were also identified, as presented in Figures 2a-2d. By employing high-level quantum chemical calculations (Figure 2e), the potential energy surfaces for both the unimolecular and H-assisted decomposition of 1-indanone have been first comprehensively elucidated. The calculation results revealed the underlying mechanisms governing the formation of two major products, styrene and indenyl radical. Styrene predominantly originates from the ring-opening and isomerization/dissociation reactions of the C_9H_9O adduct, while indenyl radicals arise from the elimination reactions occurring on the cyclopenta-fused ring, or from secondary reactions between indene and OH.

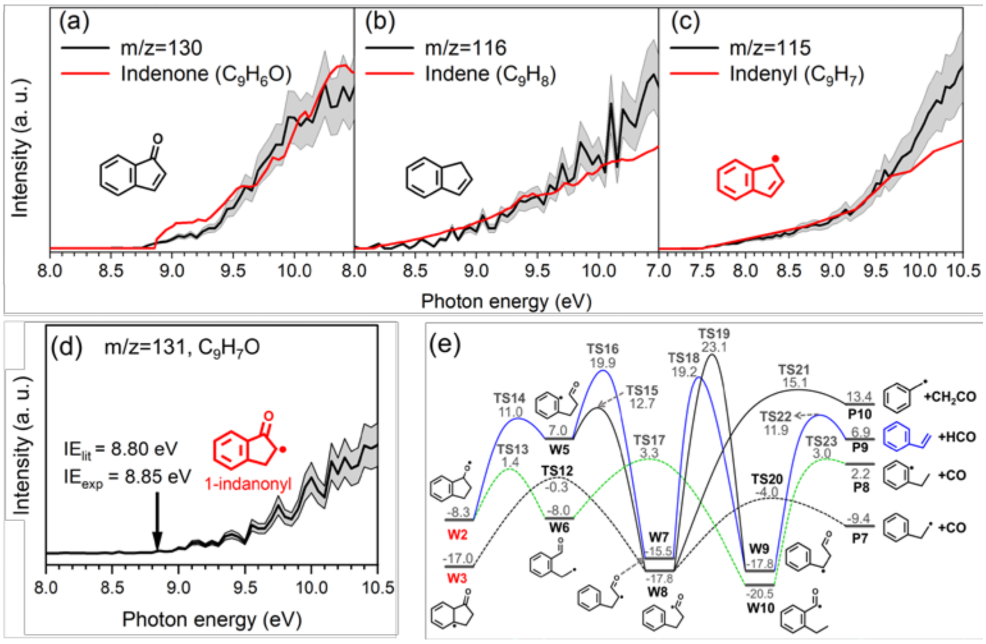

Figure 2. (a)-(d) Photoionization efficiency spectrum measured in the pyrolysis of 1-indanone in a micro flow reactor at 0.08 atm; (e) Potential energy surface profiles for the ring-opening pathways of C_9H_9O radcials calculated at the CCSD(T)-F12/cc-pVDZ-f12//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) level of theory [6].

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Speaker Biography

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Chemistry in Detonation Wave

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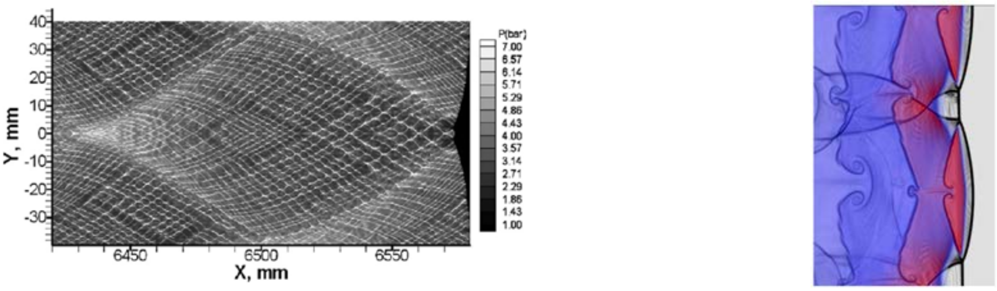
Introduction

Detonations are supersonic combustion waves whose study is relevant to industrial safety, propulsion, super-knock, and fundamental knowledge. The thermodynamic conditions behind the leading shock are extreme, which leads to ignition delay-time on the order of one ms or less, corresponding to induction zone lengths of less than a mm. Such short time-/length-scale impose stringent constrains for the numerical and experimental investigation of detonation. This abstract gives an overview of the strategies commonly employed to model chemistry in detonation. In addition, the potential of several experimental techniques in providing quantitative data for detonation simulation validation are discussed.

Strategies to model chemistry in detonation wave

A variety of models can be considered for performing numerical simulation of detonation. Steady, quasi-steady, and quasi-unsteady models are essentially zero-dimensional (0-D) reactors. For these cases, detailed reaction mechanisms can be utilized without much restriction for most fuels commonly considered in detonation studies. More relevant to the present discussion are numerical simulations of unsteady detonation wave, which require to discretize the governing equations in one, two, or three dimensions. In order to perform high-resolution numerical simulations, several approaches can be employed to describe the chemical kinetics.



(a) Double cellular structure obtained with a 2-step global model [2]

(b) OH fluorescence intensity field obtained using a reduced chemical model and a LIF model [5]

Figure 1. Examples of simulated 2-D detonation waves.

Due to the high resolution required to resolve the detonation structure, most numerical studies on detonation have relied on global reaction models, which typically include one to five chemical steps. While the simplest reaction model, i.e., the 1-step irreversible Arrhenius kinetic model, remains valuable for comparison with theoretical results, performing parametric studies, and its low computational cost, it does not allow to reproduce some important features of the combustion process, including the induction period, and the chain-branching process. Progressively including additional steps allows to derive more and more realistic chemical models, and complex behaviors can be captured, including changes of activation energy with temperature [1], or multi-step heat release profiles, which can lead to double cellular structures, Fig. 1 (a) [2]. Different approaches can be employed to establish global reaction models: (i) developing a model that closely reproduces the characteristics of the combustion process as predicted by a detailed reaction model [3]; (ii) adjusting the thermo-kinetic parameters to match the experimental cell size data [4]; and (iii) developing a global model that can reproduce the velocity-curvature curve predicted by a detailed reaction mechanism [3].

While global reaction models can provide insights into the general dynamics of detonation, there are circumstances in which more comprehensive reaction models are required. This is the case for example when predictive simulations are desired or when direct comparison with experimental planar laser-induced fluorescence (PLIF) results is performed, Fig. 1 (b) [5]. In this case, reduced or detailed reaction mechanisms must be employed. While using a detailed model for simulating detonation in hydrogen-oxygen mixtures is possible, it is usually very computationally expensive to do so for other mixtures. Therefore, reduced models need to be developed for detonation-specific conditions. It should be acknowledged that detailed reaction models are never fully validated under detonation relevant conditions. While the post-shock conditions can be reproduced in shock tube experiment, the dilution would then be much larger than for mixtures commonly used for detonation studies, so that the ignition delay-time is long enough to be measured with reasonable accuracy. Global and reduced models derived from detailed chemistry would have the same limitation.

More advanced modeling approaches include the effects of thermal non-equilibrium with a multi-temperature [6], or a state-to-state model [7]. While the former approach only requires adding a limited number of equations to describe the transfers between the energy modes, the latter requires to include one mass-conservation equation for each vibrational energy level of each molecule, leading to extremely large reaction models of limited practical relevance. These approaches have been essentially applied to hydrogen-oxygen/air mixtures.

Experimental techniques for quantitative measurements

Most experimental studies on detonation rely on the soot foil technique [8] or on schlieren visualization [9]. While providing insights into the structure and dynamics of detonation, the usefulness of these two techniques is essentially limited to qualitative validation of numerical simulations. In particular, it is difficult to infer chemical kinetic information from these data. The cellular pattern captured using soot foil corresponds to a global parameter and may exhibit important irregularity. The schlieren technique can potentially provide an indication of the induction zone length, but only for marginal detonation in narrow channels. Otherwise, schlieren does not provide quantitative information on the density gradient field. Two experimental techniques could provide quantitative information that would help validating reaction mechanisms under detonation-relevant conditions. The first corresponds to Rayleigh scattering imaging, Fig. 2 (a) [10]. With this technique, the density field can be directly measured, based on a calibration obtained using non-reactive normal shocks. The second relies on NO-PLIF. Since NO is typically not naturally present in the initial mixture, it is required to seed few thousands ppm of NO in the fresh mixture. The changes of density across the leading shock, and as the heat release occurs, allow to measure the induction zone length, Fig. 2 (b) [11].

Rayleigh scattering [11]

(b) NO-PLIF [12]

Figure 2. Two experimental techniques providing quantitative information on detonation wave.

Conclusion

Concerning numerical simulations, most approaches that can be employed to describe chemical kinetics enable to capture the main dynamics of detonation. However, to obtain predictive simulations or to study the details of the structure, the use of realistic reduced chemical models is required. Additional experimental measurements of detonation wave features are needed to better validate these chemical models.

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Speaker Biography

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Advanced methods for flame propagation in spherically expanding configuration

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1. Introduction

The simulation of complex combustion phenomena requires the definition of the fuel properties as experimentally and/or numerically determined. Among such properties, the speed at which a flame propagates through the combustible mixture at defined initial conditions constitutes a key variable in most applications, from modeling of fires and free flames to optimization of combustor functioning and performance. The flame propagation speed depends on several chemical and physical processes whose influence needs to be accurately evaluated. Function of the fuel/oxidizer mixture reactivity and of the transport properties, the laminar flame speed S_L^0 is the fundamental parameter used for chemical kinetic model validation as well as a normalizing parameter in turbulent flame models. In addition, depending on the fuel and thermodynamic conditions, the flame can accelerate due to instabilities which modify the structure of the flame and the curvature effect on this latter compared to the smooth flame. Finally, the relationship between the local laminar flame speed and the turbulence level through the root mean square (rms) velocity of the fresh gas, u', and the integral length scale, L, is crucial for accurately predicting the turbulent burning speed S_T. The present contribution focuses on recent advances in the use of spherical reactors for flame propagation studies.

2. Laminar flames

Laminar flames in expanding configuration can be used to measure laminar flame speeds through extrapolation to zero-stretch conditions. Different extrapolation methods have been proposed and analyzed in detail in literature works and nowadays their use is well established, solving long-standing controversies concerning the accuracy of the method. Nevertheless, other important aspects need to be considered to assure reduced uncertainties (of the order of 1 cm/s) as essential for kinetic model development [1]. One of the key features of the different set-ups is the size of the reactor, which indirectly affects the data range (radius domain) used for extrapolation. Measurement of relatively large flames not only reduces the uncertainties associated to the selection of the extrapolation method, but it is also mandatory for specific fuels and conditions where the linearity between propagation speed and stretch develops at large flame radii [2]. Recent measurements performed at ICARE on ammonia in oxygen-enriched air (Figure 1) provide an example of facility size effects [3]. In this case, the ICARE results were obtained in a 56-liters spherical reactor, with optical access of 97 mm, and they are compared with the data from the literature in a 4.2-liters reactor [4]. When treated in the same spatial domain as in [4], the ICARE data provide similar underestimated laminar flame speeds as in the literature (blue crosses). The size of the reactor clearly determines the large observed discrepancies. Moreover, comparing the results from the 56 and the 93 L vessels led to similar results as shown in Figure 1.

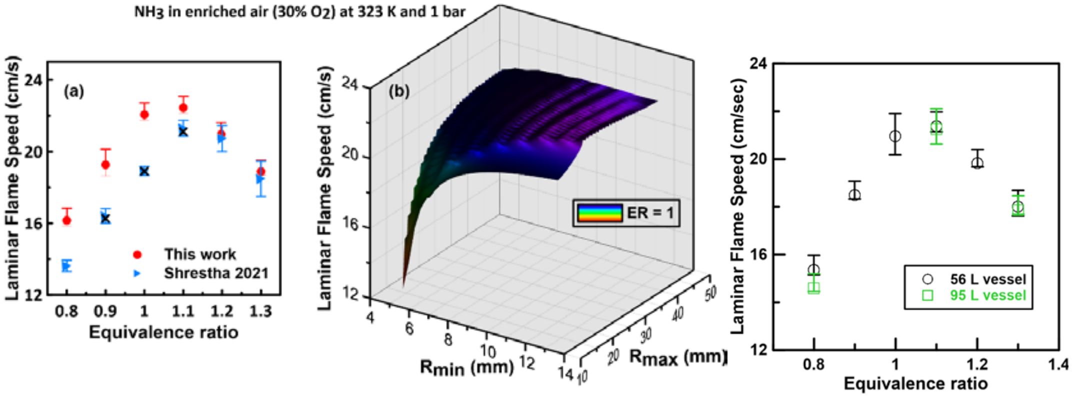

Figure 1. Laminar flame speeds of ammonia/enriched air (30% O_2) mixture at P_{in} = 1 bar and T_{in} = 323 K.

Radiation-induced effects can also provide a source of uncertainty in the laminar flame speed measurements, especially at high pressures and in the presence of unburned mixtures and combustion products characterized by strong radiation absorption/emission (CO_2, H_2O, soot, etc.). In non-stationary flames, experimental measurements of radiative heat losses are challenging, and the radiative heat losses have been conventionally estimated by theoretical models. The new instrument FAIRS (Fast Absolute InfraRed Sensor, [5]) was developed at ICARE for absolute, real-time radiation measurements. The method is based on re-emission from a thin blackbody-like material composed of carbon nanotubes following thermal radiation absorption. The sensor, calibrated with a standardized blackbody, shows a response time of 1 µs, as required for monitoring expanding or accelerated flames. Typical results for CH_4/air mixtures are presented in Figure 2. These results are essential for validation of the theoretical models in practical applications.

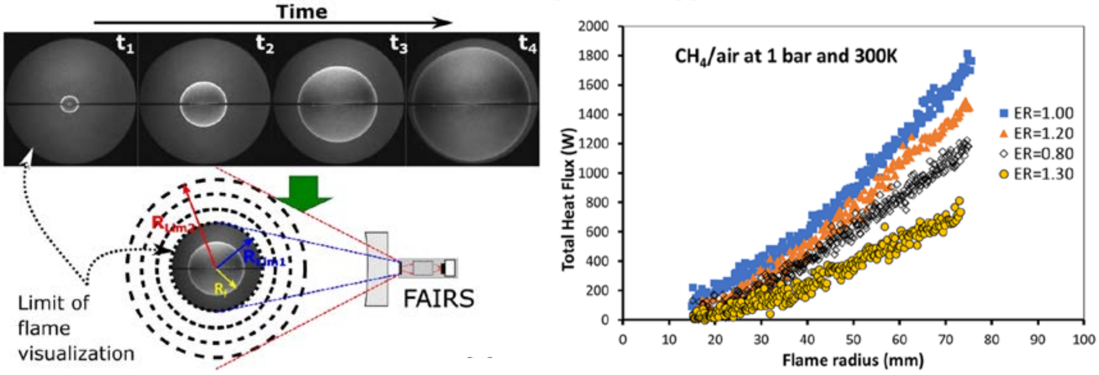

Figure 2. Schematic of FAIRS and absolute measurements performed at ICARE on methane expanding flames.

3. Turbulent flames

Turbulent flames are of great interest for different industrial applications as well as for the explosion risk assessment. Spherical expanding flames in a well-characterized environment are good examples for understanding the effect of the turbulence on flame propagation including for near limit flames which are dominated by buoyancy that cannot be addressed otherwise as they are unstable and difficult to stabilize in a burner configuration. At ICARE, a 93 L vessel equipped with 8 fans is used to generate a homogeneous and isotropic turbulence over a large domain allowing the measurement in well-characterized turbulence up to a radius of 200 mm [6]. The ability of measuring the turbulent flame speed over a large domain in well-controlled environment sheds light on the variation of the turbulent flame speed versus the turbulent intensity as function of the flame size, allowing thus for the instabilities to develop and interact with the turbulence (figure 3).

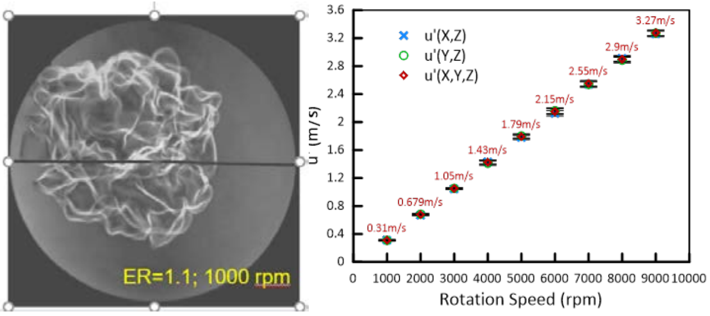

Figure 3: Example of turbulent flames for ammonia/air mixtures, initially at 1 bar and 309 K, for an equivalence ratio of 1.1. The fan rotation speed was fixed at 1000 rpm corresponding to u'=0.31 m/s.

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Speaker Biography

Nabiha Chaumeix is a Senior Scientist and Director of the laboratory ICARE - CNRS in Orléans, France. She obtained a PhD in 1993 in Mechanical Engineering from the University of Orléans, France. After graduation, Nabiha did a postdoc at Caltech, USA, in Professor Shepherd’s group, focusing her research on unsteady jet ignition, before re-joining the laboratory ICARE as a Senior Scientist in Professor Paillard’s group. Nabiha’s research interests are related to: (i) high temperature chemical kinetics using shock tubes and soot formation from heavy fuels; (ii) the determination of the combustion fundamental properties such as flammability limits, laminar flame velocities, auto-ignition delay times, detonation characteristics (cell size, detonation speed, etc.) and the development of detailed chemical kinetics applicable to these phenomena; (iii) assessment of safety explosion criteria with the detailed study of flame acceleration covering both subsonic and supersonic flames.

Topic 3. Plasma combustion: experiments and modelling

Keynote presentation

Plasma-assisted combustion experiments and modeling: challenges, advances, and opportunities

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Challenges and advances

Over the past years, significant advances have been made in the understanding of plasma-assisted combustion phenomena. Furthermore, applications in this field have expanded from ignition and heat-release enhancement to extension of lean-burn and blow-off limits, flame and thermo-acoustic stabilization, in-situ fuel reforming and ozone synthesis, flow control and space propulsion, and many more [1–6]. Nevertheless, a thorough fundamental understanding of various key underlying physicochemical processes has not yet been achieved.

From an experimental point of view, some of the key challenges are related to obtaining accurate data without interference effects from the plasma discharge. The two main difficulties discussed here are the effect of diluting/balance gases and measuring the reduced electric field (E/N).

Effect of diluting/balance gases

Whereas in traditional chemistry, He and Ar (and N_2 to a certain extent) can be considered as inert gases that do not take part in chemical processes, in a plasma discharge, the presence of these gases can significantly affect chemical processes—and, thus, they cannot be considered chemically inert [7]. When electrons collide with these species, they can become electronically excited. Through subsequent quenching reactions, they can transfer their high internal energy directly through penning-dissociation and -ionization reactions [7,8], or indirectly through fast gas heating [9]. Hence, to study plasma-assisted processes, new standardized methods for undiluted conditions need to be developed and evaluated [7,10].

Measuring and controlling the reduced electric field (E/N)

The E/N determines the electron energy distribution function (EEDF) and, potentially more important, the fraction of electron energy transferred to the different electron-neutral collision processes (i.e. elastic, vibrational and electronic excitation, dissociation, (dissociative) ionization, dissociative electron attachment) [10, 11]. Hence, depending on the value of E/N, the electron-induced chemistry can be vastly different for the same operating conditions [8, 10]. Therefore, accurate E/N values are essential for further model validations. Although significant experimental advances have been made (i.e. E-FISH [6]), several obstacles remain.

From a modeling point of view, some of the key challenges are related to the availability—or rather, lack thereof—of three different types of data: (i) cross section data for electron collisions, (ii) chemical kinetic data for low- to mid-temperatures, and (iii) reaction data for excited species.

Cross section data for electron collisions

There are significant constraints with respect to the available cross section data for electron collisions. Typically, there is no data available for the larger molecules ($> C_3$) that are of interest to the energy and combustion community; and even for basic molecules, like O_2, the commonly used data appears inaccurate [12]. A major issue is the dwindling effort to obtain this data experimentally. This is leading to the loss of essential knowledge, at a time when validating old data and measuring new data are essential. Luckily, recent developments make it possible to compute theoretical cross section data sets with satisfactory agreement within a short time frame [11]. Nevertheless, this approach would benefit from additional experimental validation.

Chemical kinetic data for low- to mid-temperatures

While the high-temperature chemical kinetics ($T_g > 1000$ K) are relatively well understood and captured by existing reaction mechanisms, the mid- to low-temperature chemical kinetics between room temperature to $T_g = 1000$ K are not well-established—not even for the first building block of any combustion mechanism, H_2/O_2. Through combined experimental and modeling studies for undiluted hydrogen mixtures, it became apparent that especially the HO_2-related chemistry exhibits major inconsistencies in this temperature-range [10]. Since HO_2 plays a central role in any combustion process, this is the key element that requires improvement to obtain a more fundamental insight. Recent measurements of $[HO_2]$ in plasma discharges [13] and improved reaction rates from computational methods [14–16] are essential steps towards developing accurate mechanisms.

Reaction data for excited species

The production of various (long-lived) excited species in plasma discharges requires additional reaction data for the most prominent of these excited species. Excited species, especially electronically excited species, typically have a large internal energy and, therefore, reactions with these species have lower activation energy barriers and higher rate constants compared to their ground state equivalents. Significant efforts have been made in the past to determine reaction rate data for the main electronic excited species of oxygen (i.e. $O(^1D)$ and $O_2(a\ ^1\Delta_g)$) and nitrogen (i.e. $N_2(A\ ^3\Sigma_u^+)$ and $N_2(a\ ^1\Pi_g)$) [2]. However, this data typically lacks temperature dependent information and reaction rates for quenching with larger molecules are missing.

Opportunities and outlook

Major opportunities to accelerate advances in the field of plasma-assisted combustion are accessible through:

(i) Collaborations between the high-temperature combustion and low-temperature plasma communities. In essence, both are studying reactive flows; one sustained thermally and the other electrically. As a result, there is a strong synergistic overlap in the methods and approaches used in both communities (e.g. optical diagnostics, modeling tools). Joint efforts could accelerate the development of comprehensive methods.

(ii) Advances in computational methods. The increased capabilities and fidelity of quantum chemistry-based ab-initio methods opens the door to the relatively fast generation of (currently unavailable) essential data for the development of comprehensive reaction mechanisms (including electron and excited species reaction rates and fragmentation patterns). Note that additional experimental validation is preferred for overall robustness.

(iii) Development of standardized methods. Standardized measurement, (accessible) data reporting, and modeling frameworks tailored to the challenges of plasma-assisted combustion research and based on the best practices used for traditional combustion research, could significantly advance knowledge in the field and overcome the existing fragmentation of reactor designs, reaction mechanisms, and in-house proprietary codes.

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Speaker Biography

Ramses Snoeckx is an interdisciplinary plasma scientist whose research focuses on the underlying plasma-chemical kinetics of plasma processes for energy and environmental applications. He received his PhD in Chemistry (2017) summa cum laude with the congratulations of the examination committee from the University of Antwerp. The International Plasma Chemistry Society granted him the Young Investigator Award for his research on the plasma-based conversion of greenhouse gases into value-added chemicals and fuels. Snoeckx has collaborated internationally through research visits at University College London, Seoul National University, Drexel University, and University of Lisbon. Until early 2024, he was a Research Scientist at the King Abdullah University of Science and Technology (KAUST). Currently, he holds the positions of Scientist and Project Leader in the Materials Meet Life Department at Empa, the Swiss Federal Laboratories for Materials Science and Technology.

Invited presentations

Ignition enhancement and NO_x formation of NH_3/air mixtures by non-equilibrium plasma discharge

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This work studies plasma assisted low temperature NH_3/air ignition and NO_x formation in a repetitively-pulsed nanosecond discharge at atmospheric pressure by using an experimentally-validated plasma-combustion kinetic model [1]. The results show that plasma discharge significantly enhances low temperature NH_3 oxidation and ignition. Compared with thermal ignition, the ignition delay time is shortened by 2-5 orders of magnitude due to the kinetic enhancement of excited species and radicals. The radicals (NH_2, NH, H and O) produced through electron impact dissociation and quenching of electronically excited N_2^*, $O(^1D)$ and $N(^2D)$ promote OH production and further accelerate NH_3 oxidation. The results show that there exists a non-monotonic dependence of ignition delay time on the reduced electric field strength. The optimum ignition enhancement is achieved at 250 Td at which the production of electronically excited species and radicals is most efficient. The vibrationally excited species produced at lower electric fields (<100 Td) are less effective in enhancing ignition because they only induce gas heating through the fast vibrational-translational relaxation by NH_3 and H_2O. At a higher electric field, although the efficient production of NH_2, NH, H, O and OH by plasma creates new low temperature reaction pathways in enhancing low temperature NH_3 ignition, the ignition is inhibited through $NH + NO = N_2O + H$ and chain-termination reaction $NH_2 + HO_2 = NH_3 + O_2$. The ignition delay times at different equivalence ratios show that the ignition enhancement by plasma is more effective at fuel-lean conditions due to the faster generation of $N_2(B)$, $O(^1D)$ and O from air, leading to accelerated NH_3 oxidation via $O(^1D) + NH_3 \rightarrow NH_2 + OH$, $NH_3 + O = NH_2 + OH$ and $NH_2 + O = NH + OH$. The sensitivity analysis shows that the reactions involving O and $O(^1D)$ production are more effective on NH_3 ignition enhancement than the fuel dissociation by electrons. Moreover, the ignition is also enhanced by NO_x formation in plasma via reactions $NH_2 + NO = NNH + OH$ and $NO + HO_2 = NO_2 + OH$. This work advances the understanding of non-equilibrium excitation and NO_x formation by plasma discharge on low temperature NH_3 ignition [2].

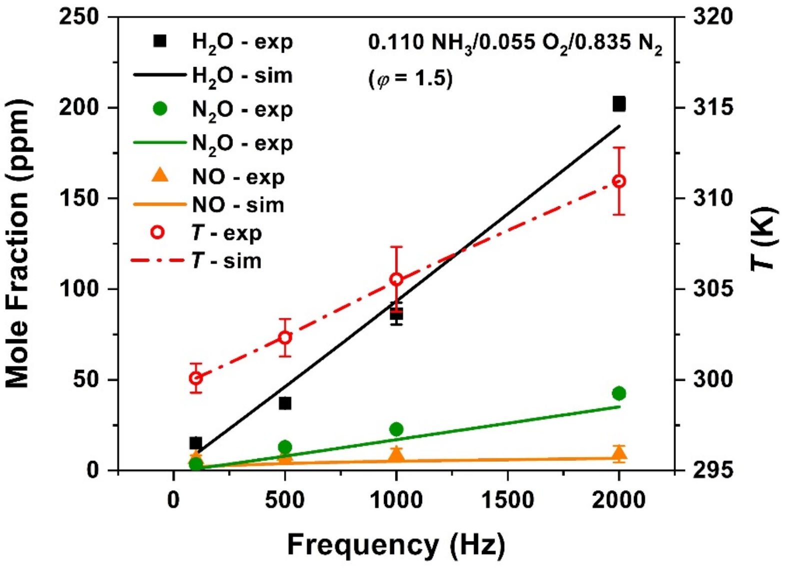

Figure 1. Comparison of species concentrations between experimental measurements and model predictions with a continuous discharge at 100-2000 Hz.

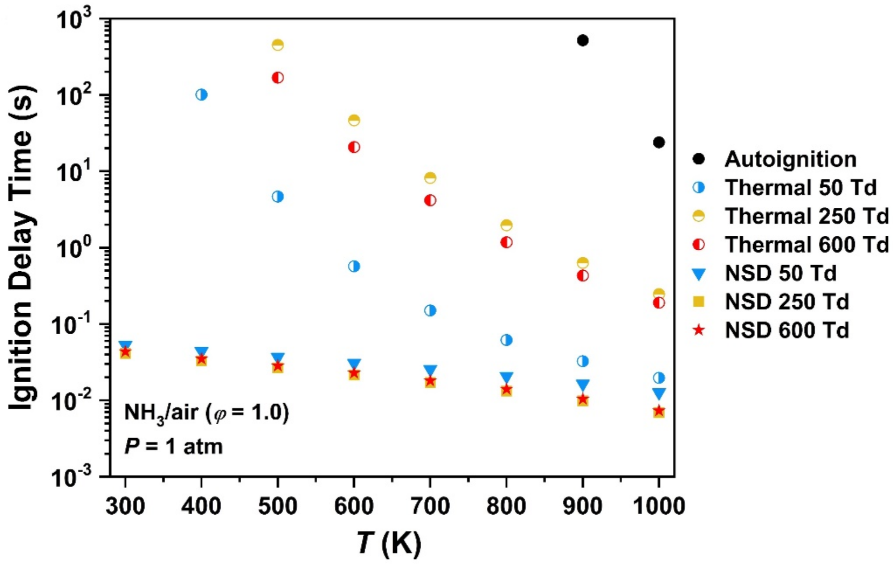

Figure 2. Ignition delay times for autoignition, thermal ignition and NSD assisted ignition with different E/N as a function of temperature.

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Speaker Biography

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Ignition of ionic liquid and metal fuels using a microwave plasma torch

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With the increasing demand for sustainable, low-carbon energy, combustion technology is exploring green fuels like ammonia, hydrogen, metal fuel and others[1]. These differ fundamentally from traditional fossil fuels, presenting new challenges for the adaptability of existing combustion technologies. Against this backdrop, plasma assisted combustion may offer new ideas for the innovation of combustion systems[2]. This work designs a microwave plasma actuator to burn different kinds of fuels, specifically tailored for the rapid ignition of ionic liquid propellants and aluminum metal fuels. The application of this technology is expected to enhance combustion efficiency and further promote the widespread adoption of green fuels in practical applications.

Microwave plasma actuator

Figure 1a shows images of the copper-constructed actuator. The fuel tube passes through a copper ring, which is connected to a coaxial cable. Microwave radiation at 2.45 GHz, generated by a solid-state source, is directed to the resonant cavity via the coaxial cable. To enhance flame stability, an extra gas flow is asymmetrically directed into the cavity, creating a mild swirl around the central tube. The plasma torch synergizes electromagnetic energy with the gas surrounding the tip of the tube, where the electric field is amplified to accelerate electrons and trigger plasma ignition. The compact design of the ¼-λ resonant cavity, improvement of the quality factor (QF) of the MW igniter, and precise tuning according to plasma impedance (w/o. propellant) make the device more efficient and thus allow the fuel to ignite at low power.

Figure 1b presents the emission spectra of an air plasma torch operating at a flow rate of 1.5 L/min, with the forward power maintained at about 100 W and the reflected power below 10 W. The spectrometer captures broad-band emissions from $N_2(C)$ within 320-390 nm, which indicates the hot region of the plasma torch. Fitting the (1,2) and (0,1) bands peaking at around 353.7 to 357.8 nm shows that the rotational temperature is T_{rot}=(2000±200) K and the vibrational temperature is T_{vib}=(4800±500) K, indicating both ohmic heating and nonequilibrium plasma effects. The high vibrational temperature suggests electronic and vibrational excitation of nitrogen molecules. At atmospheric pressure, the peak temperature at the torch center can be assessed by $T_{torch} \approx T_{rot}$ =(2000±200) K due to fast rotational-translational relaxation.

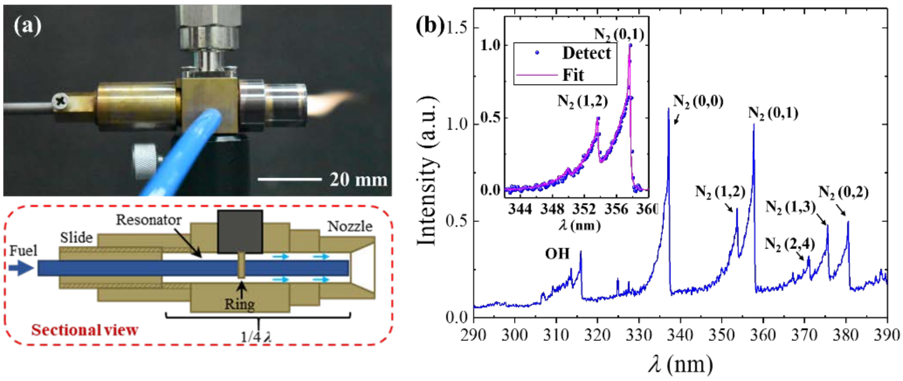

Figure 1. (a) Image and schematic of the microwave plasma actuator (b) typical emission spectra from the air plasma torch

Ignition of ionic liquid dual-mode monopropellant

The blend of hydroxylammonium nitrate (HAN) and imidazole-based ionic liquid has shown good feasibility in chemical and electric dual-mode green space propulsion[3]. As conventional catalyst-driven ignition faces challenges arising from long pre-heat delay and catalyst failure, this work uses the plasma-assisted microwave torch to ignite the ionic liquid monopropellant in multi-start operations. Figures 2a and 2b show that the actuator ignites propellants with ~100 W input power, and currently the plasma torch can ignite the propellant in multi-start operations with a flow rate exceeding ~42 g/min, corresponding to 1 N thrusters.

Regarding the ignition mechanism, the electrode tube has a temperature higher than 100 °C and evaporates the water in the propellant to accelerate flowing and even leads to droplet spurting. Spectra fitting of $N_2(C)$ indicates that the gas temperature of the torch center reaches 2000 K. The HAN and [Emim][EtSO4] ionic liquids decompose quickly at such a high temperature, and the small intermediate species form gaseous flame that has been identified by the OH PLIF imaging. The non-equilibrium plasma will also accelerate the gaseous burning through kinetic effects of excited species. Another important role of plasma is that copper atoms produced by plasma erosion have a catalytic effect on the decomposition of ionic liquids, thus accelerating the overall reaction. The participation of copper atoms has been verified by the green light emission and energy spectrum analysis of the burning residue. Differing from the kinetic enhancement through electron impacts with conventional molecular fuels, this is a new pathway of plasma-assisted combustion for ionic liquid fuels.

Ignition of aluminum powder fuel

Focused on the zero-carbon metal fuel concept[4], this research employs a microwave plasma actuator to rapidly ignite and sustain the combustion of micron-sized aluminum particles. Typically, the ignition of such aluminum particles requires temperatures exceeding 2000 K, critical for the melting, cracking, or phase transition of the aluminum oxide layer that encapsulates the particles. Consequently, the microwave plasma torch, with its gas temperature of approximately 2000K as deduced from nitrogen spectral analysis, markedly aids in igniting aluminum particles by triggering various transitions of the oxide layer that hinder aluminum oxidation.

Figures 2c-2f display the stabilized aluminum combustion flames using the microwave plasma torch at varying powder densities. As the particle density increases, the combustion mechanism of a single particle transforms into group combustion with a large-scale flame sheet. Spectral analysis of Al atomic spectra and AlO molecule bands indicates the selective coupling of microwave energy with localized aluminum flames, due to the superfocusing of microwave radiation on extremely subwavelength scales. The microwave plasma actuator not only shortens ignition delays but also enhances flame stability. This is pivotal as aluminum stands out as a candidate for zero-carbon, high-energy-density fuels in external combustion engines or powder ramjets. Moreover, further tests show that aluminum particles can be ignited using a CO_2 plasma torch, which indicates the potential for negative-carbon emissions, presenting a promising strategy for greenhouse gas reduction when integrated with carbon capture and storage (CCS) technologies.

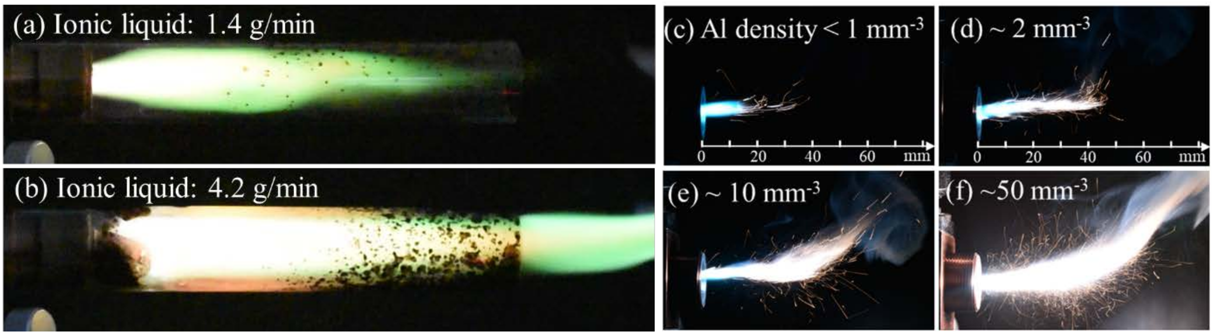

Figure 2. Plasma-assisted combustion images: (a-b) ionic liquid propellant with different fuel flow rates, and (c-f) aluminum powder jets with varying initial particle number densities.

Acknowledgements

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Speaker Biography

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Plasma assisted ammonia combustion: opportunity and challenge - It is not just a simple switch of fuel

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It might be better to start off the discussion from the history of plasma assisted combustion. The application of non-equilibrium plasma started to draw significant attention since about thirty years ago. Specifically, with the availability of non-equilibrium plasma sources, such as nano-second pulsed high voltage power supply, significant research progress has been made to explore the kinetic effect rather than thermal effect on combustion. This is because kinetic effect could be more selective and efficient comparing to thermal effect. Kinetic effect, for example, the production of atomic oxygen from plasma can enhance specific reactions therefore enhance the flame. Thermal effect will enhance almost all temperature sensitive reactions without selection. With the advancement of optical diagnostics and modeling, our understanding on radical productions from plasma and their effect on combustion significantly improved in the past decades.

In recent decade, hydrogen economy is again drawing global attention as part of a technology-based approach to reduce global carbon emissions. The Paris Climate Agreement set targets for decarbonization across numerous sectors [1]. To power propulsion systems and generate electricity, hydrogen and its carbon neutral carrier, such as ammonia, become to be the focus of fuel related research from its production to end application. Given logistic challenges on its volumetric energy density, safety of handling and storage, the application of hydrogen as energy source is significantly limited. Therefore, the research interest of using ammonia as fuel starts to rise very quickly, either as a carbon-free alternative fuel or hydrogen carrier. Although increasingly fast since 2020, the number of papers on plasma assisted ammonia combustion are still limited. This discussion is aimed to prepare and inspire more future studies towards the application of plasma on zero carbon fuels in the future. Ammonia was investigated from the 1940s to 1960s as an alternative fuel [2, 3]. It was concluded that pure ammonia could not be used as fuel for gas turbines due to its poor flame stability. In addition, ammonia combustion has very narrow flammability range, low laminar flame speeds, and features very high NOx emission owing to the fuel-bound nitrogen. Therefore, ammonia combustion was not pursued for several decades. Towards all the challenges that ammonia combustion faces except the NOx emission issue, plasma naturally seems to be a promising solution to enhance ammonia ignition and flame. It is well known that plasma could enhance ignitions, flame propagation speeds, improve flame stabilization and extend flame extinction strain rates and lean blowoff limits (LBO) for all hydrocarbon fuels. Could plasma enhance ammonia combustion? It is also reported that plasma could increase NOx emission for hydrocarbon fueled combustion. Would plasma further increase NOx emission in ammonia combustion?

Before the first experimental exploration was conducted, there existed two numerical explorations. Shioyoke et al. [4] conducted numerical simulation and reported the increase in laminar burning velocity of ammonia flames with addition of plasma generated species (H, O and OH). They concluded that the increase in OH produced by plasma accelerated flame propagation. Faingold and Lefkowitz [5] numerically studied ignition delays of ammonia/oxygen/helium mixtures and reported reduced ignition delays under plasma activation owing to plasma created species (H, O and OH). Choe et al. [6] conducted the first experimental exploration on plasma assisted ammonia flame and simultaneous reduction of NOx emission and extension of lean blowoff limits of ammonia/air flames with the activation of nano-second pulsed plasma were reported in 2021. NH2* chemiluminescence was among one of the first optical diagnostic techniques used to study plasma assisted ammonia combustion.

Given this research background, I foresee a few challenges and opportunities for the investigation of plasma assisted ammonia combustion.

1. New phenomena: Given the infancy of this research topic, large number of new phenomena are still in need of exploration besides lean blow off limits and NOx emissions. It is highly possible that mixture of ammonia and other fuels, such as hydrogen will be used as fuel. There might be synergies between fuel mixtures, and between fuel kinetics and plasma kinetics. Would plasma have the same effect or opposite effect for such fuel mixture? I do not know. So let us do it. Exploratory work should be encouraged.
2. Unknown kinetics: Kinetics of ammonia is very complicated and completely different from hydrocarbons. It is not well understood despite huge effort on ammonia combustion. Our recent work [7] on

ammonia kinetics showed that none of existing kinetic models could predict autoignition delays of ammonia. It makes understanding of plasma ammonia assisted combustion even more challenging especially for numerical investigations. Moreover, ammonia plasma itself is rarely studied even it has broad applications.

3. Limited diagnostic techniques: OH radical is still important but may not be the most reliable one to mark ammonia flame front [8] even though it is the most commonly measured radical. Alternatively, NH and NH_2 should be measured but these techniques are not wildly available. The missing of carbon in the system also disabled carbon containing species-based method, such as LIF of CH or CH_2O. NO is a critical intermediate species and NO LIF in ammonia containing environment requires a new laser wavelength because conventional NO LIF utilizes 226 nm to excite NO molecules but NH_3 has strong absorption at the same wavelength. Ammonia combustion releases N_2O which is a potent greenhouse gas. Its measurement is still challenging except sampling. Owing to the low reactivity of NH_3, NH_3 slip from flame is also a concern for practical applications. Therefore, measuring NH_3 is important.
4. Change of transport property: plasma could decompose NH_3 into H_2. Hydrogen has very high diffusivity therefore changing the transport properties of both flame and plasma itself. It is unknow what are the potential effects of such change of transport properties on flames and plasma discharge. Would H_2 production also improve the uniformity of plasma?
5. Fuel flexibility: for future carbon free alternative fuels, the composition of the fuel may fluctuate depending on the source of the fuel. For example, if cracked ammonia is used as the fuel, the H_2 content may fluctuate. How could plasma help?
6. Challenges on high pressure: as a long-term challenge, we need to be innovative (easy for you to say) towards high pressure applications of plasma in combustion systems.

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Speaker Biography

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Integrating plasma effects into simulations of real combustors: status and challenges

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Plasma-Assisted Combustion (PAC) is an emerging technology to enhance the ignition and flame stabilization processes in combustion systems. This technology holds promise for enhancing the window of operation of practical combustors [1-8]. However, the design of the system requires a fundamental understanding of the processes involved in improving combustion. For this, multi-physics high-performance simulation plays a key role. Integrating PAC effects into simulations of real combustors is a complex yet crucial step towards the practical implementation of this technology.

PAC simulations in real complex configurations are highly challenging and therefore quite rare. Despite the recent efforts to reduce Non Equilibrium Plasma (NEP) chemical kinetics [9-11], the computational cost of solving the electric field, the electron energy, the continuity equations for charged and excited species, in addition to the Navier–Stokes equations for reactive flows is very high. The integration of NEP effects in 3D simulations of turbulent reactive flows inside complex geometries can only be achieved with simplified models that incorporate all relevant plasma effects for the considered study. Such a model has been developed by Castela et al. [12] for nanosecond discharges, incorporating the most important effects of NEP in a N_2/O_2 mixture. In this model, the relaxation of electronically excited N_2 molecules translates into a fast increase of the gas temperature and into the fast dissociation of O_2 molecules, whereas the relaxation of vibrationally excited N2 molecules translates into a slower heat release. The model has been successfully applied to analyze the flow induced by a plasma discharge in a Direct Numerical Simulation (DNS) framework [13]. It has also been successfully applied in a Large Eddy Simulation (LES) framework to study turbulent flame ignition [14] and turbulent combustion enhancement [5, 15]. Although this simple model has proved very effective, it does not include the effects of a variation in the reduced electric field, nor does it take into account the secondary effects that can lead to the production of pollutants. Therefore, Barléon et al. [16] have extended the phenomenological approach of Castela et al. [12] to systematically compute branching coefficients and take into account more plasma processes involved in methane-air mixtures, including the production of N and NO, which is crucial for the study of NOx formation. This extended model has been successfully used to study flame stabilization [7, 16] and NOx formation [17]. Based on the same principle, another model has been recently derived for ammonia-air mixtures [18].

Despite these efforts, many phenomena are still very complex to model.

- Pulse-to-pulse effects: When high-frequency Nanosecond Repetitively Pulsed Discharges (NRPD) are applied, the discharges may take place in an environment impacted by the previous discharge. In such a case, the composition of the mixture is uncertain, the discharge channel can vary, and the gas number density varies. It has also been found that several discharge channels are formed and the deposited energy is distributed over several branches during one pulse [4]. These variations can give rise to a transition from glow to spark regime and have a major impact on plasma effects. Sophisticated models are required to consider these phenomena.
- Uncontrolled discharge location: In certain electrode configurations, such as parallel bars [1] or an electrode in the center of a swirler [2], the discharge position is dependent on the most favorable conditions and therefore varies spatially with the flow. This is a modeling challenge that needs to be solved by developing reduced models to estimate the most probable location of a discharge in a turbulent flow. Barléon et al. have overcome this problem by developing an empirical model that reproduces experimental observations on a swirled burner [19]. This was possible because the position of the discharges followed a certain logic: a first discharge was initiated at a random position, and several successive discharges followed the trace of the previous one in a rotating motion around the burner axis.
- High-pressure discharge characterization: There is a lack of literature on the characterization of plasma discharges at high pressure. However, real engines operate at high pressure, and we need to develop the technology for practical applications. The plasma regime could more easily transition from glow to spark-type discharges at high pressure. Spark discharges have a high neutral gas temperature and electron number density, but a low electron temperature. It consumes a large amount of energy and has less kinetic enhancement effect

in combustion compared to NEP [20]. Reduced model must be reworked to account for this regime. Besides, the development of experimentally validated high-pressure plasma assisted combustion kinetic mechanism is needed. The current plasma-combustion kinetic model cannot predict key intermediate species at low temperature and high-pressure conditions. Many reaction pathways and rate constants are still missing [20].

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Speaker Biography

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Topic 4. AI-TST-ME: automation, benchmarking and knowledge transfer.

Keynote presentation

Automation towards “big data” in ab initio theoretical kinetics: is our community ready for knowledge transfer?

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The field of theoretical kinetics applied to the study of high-temperature processes has undergone outstanding progress in the last decade, leading to extremely accurate predictions of rate parameters. Computational availability and efficiency have thus switch research focus to the automation of theoretical methodologies. This introduction reviews some of the latest advancements, inviting the community to build a shared view to fully exploit the current paradigm shift towards data-driven kinetic model generation.

1. Automation in reaction path discovery and PES exploration

The definition of the list of possible reactions occurring in a reactive system is the first step for the automatic construction of a kinetic mechanism. The most popular reaction mechanism generation codes such as KinBot [1] and Arkane/RMG [2] exploit mechanistic-based approaches, similar to implementations available in codes focused on accurate calculation of rate constants of defined pathways, such as Auto-Mech [3] and EStokTP [4]. *Mechanistic approaches work relatively good for well-known elementary reaction types, however they are less effective for less studied systems* (e.g., cyclic/aromatic and large species, heteroatoms other than C, O..). To overcome these limitations, molecular dynamics (MD)-based approaches automate trajectory simulations for reaction path discovery, such as in AutoMeKin2021/ChemDyME [5,6] and ChemTraYzer [7]. However, these protocols are sensitive to the quality of the potential, of the operating conditions, and of the collective variables chosen in the case of metadynamics simulations. Hybrid approaches are also possible: for instance, in our recent work [8] we successfully combined metadynamic-based conformer sampling (as in CREST [9]) with the growing string method for transition state search. *While at present no methodology was proven to outperform all the others and the best suited approach may be system-specific, each one requires some degree of user experience. Hence, an important perspective to maximize the use, impact, and benchmarking of the proposed automated methods is careful documentation and more programming efforts towards user-friendly tools.*

Additionally, future works should focus on *less-automated* but possibly impactful aspects of high-temperature kinetics. For instance, automated protocols for the identification of peculiar TSs such as in roaming reactions or intersystem crossing are missing in the literature. Another neglected aspect is the inclusion of *stereochemical resolution in kinetic models*; however, Elliott et al. recently presented an automated workflow to build stereochemically resolved mechanisms and proved the impact of stereochemistry on the macroscopic combustion properties of n-butane. Finally, *non-thermal effects* are another poorly explored aspect in kinetic mechanism generation; while one automated protocol for generation and estimates of prompt reactions exists [10], no similar approach -nor an appropriate CHEMKIN-like framework- exist for e.g., chemically termolecular reactions.

2. Automation and benchmarking of thermochemistry

Thermochemical properties are essential to the chemical accuracy of kinetic mechanisms and are also the field where benchmarking and automation are most advanced. Most automation approaches focus on determining accurate formation enthalpies at 298 K. Recent advancements focused on accurate calculations for large molecules -where atomization reaction schemes are less effective- through bond additivity correction approaches [11] or connectivity bond hierarchy schemes [12]. However, *benchmarking studies are mostly available for alkanes, while for different types of species (such as PAHs) both the system size and limited data availability hindered systematic and accurate calculations.* Additionally, *no accurate thermochemical properties nor automated protocols are available for transition states*. Finally, only few works have focused on benchmarking and automation of accurate computational protocols for *heat capacities and entropies for* *large species* through e.g., frequency scaling or corrections for anharmonic effects, which might be an important and interesting focus of future research.

3. Automated rate constant calculation and benchmarking

The automated codes mentioned in Section 1 are (or can be) coupled with automated routines for the calculation of rate constants based on transition state theory, generally with 1D master equation simulations. Achieving high accuracy in the derived kinetic parameters is possible but challenging. Accurate estimates for energy barriers are key: for small molecules, well-defined accessible computational protocols are defined. Larger systems instead require a higher degree of approximation. *Recent implementations of coupled cluster theory with local or frozen orbital approximations (e.g., FNO-CCSD(T)) promise very high accuracies, however they were not tested extensively on different types of molecules*. Other approaches suggest extrapolation from simpler systems through e.g, *scaling factors or machine learning techniques but are not yet fully automated*. Finally, no automation has been explored for electronic structure calculations of reactions with strong *multi-reference effects*. Other relevant aspects include the estimate of collisional energy transfer parameters, inclusion of anharmonic effects, variational and variable reaction coordinate implementation of TST. *While some automated protocols are available in the literature (e.g., in Arkane, Auto-Mech, EStokTP, Polyrate), no code provides a complete and detailed treatment of all of them, and it is often hard to predict in advance which aspect is the most relevant to the study of the system of interest*. Future integration of these codes' functionalities should be certainly encouraged.

4. AI applications to the derivation of PESs and rate constants

The increasing impact of AI-based methods on all scientific fields has encouraged their application in the field of high-temperature chemical kinetics. For instance, machine learning (ML) neural network (NN) techniques are being explored to obtain high-fidelity potentials from lower-level calculations. These methods are promising particularly where state-of-the-art methodologies are inapplicable (i.e., large systems) and are already coupled with automated PES exploration codes, such as in KinBot [13]. *However, critical and not fully benchmarked aspects in the application of these methods regard 1) quality of the training data, 2) the large (but how large?) amount of data required, 3) the potential violation of physical constraints*. In the future, it is extremely likely that ML-NN potentials will be computed routinely and fully automatically. It is therefore key to properly understand the requirements and protocols for the derivation of accurate potentials first, as well as to distinguish when and if the use of ML-NN methods is worth the effort.

5. Towards big data: can we make knowledge transfer: effective?

The increasing automation of electronic structure calculations, TS search, and kinetic mechanism generation is driving a paradigm shift towards a data-driven approach in chemical kinetics. Therefore, it would seem natural that this shift is accompanied by *proper data storage, standardization, and database construction to 1) facilitate data sharing, reproducibility, and benchmarking, 2) avoid the waste of computational power and therefore energy resources*. Thermochemistry or rate constant databases such as ATcT, NIST, or the open source RMG database provide useful sources, however all of them are updated by restricted groups of contributors. *Hardly any database is available for electronic structure calculations* for molecules (one example is QM9 database [14], a collection of DFT calculations for molecules), while *none is available for storage of transition states*. At this point, rapid progress towards data-driven approaches requires an effort from our whole community for standardization and sharing that will lead to new and still unknown prospects for chemical kinetics.

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Speaker Biography

Luna Pratali Maffei is an assistant professor at the Department of Chemistry, Materials and Chemical Engineering of Politecnico di Milano, Italy. She obtained her PhD in Industrial Chemistry and Chemical Engineering at the same university in December 2022 under the supervision of Prof. Tiziano Faravelli and Carlo Cavallotti. The focus of her PhD was the theoretical and kinetic modeling of aromatic hydrocarbons mostly targeting relevant oxidation reactions, benchmarking of theoretical methodologies, and lumping approaches for the integration of rate constants into large kinetic schemes. During her PhD, she also spent a visiting period at Argonne National Laboratory, working with Dr. Stephen Klippenstein on the automation of statistical models describing prompt effects into kinetic schemes. Her efforts and achievements in bridging fundamental chemistry and kinetic modeling were already recognized with e.g., the D'Alessio award for the best Ph.D. thesis from the Italian Section of the Combustion Institute-ASICI (2024) and with the best paper award for the gas-phase kinetics section at the 39th International Symposium of Combustion (2022). Her current research is focused on theoretical calculations for complex reactions involving aromatic hydrocarbons, rate rule development, and kinetic modeling of hydrocarbons cracking and biomass gasification processes.

Towards automated, predictive, theory-based mechanisms: *n*-butane oxidation

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Introduction

Mechanisms constructed with ab initio transition state theory-based master equation (AI-TST-ME) rate data offer unique insight into the underlying chemical processes during combustion over a wide range of conditions. Recent advances in automated thermochemistry, kinetics, and reaction network generation software [1] have made it feasible to obtain AI-TST-ME based mechanisms even for large fuels. Alongside this progress, arises the challenge of understanding the uncertainties within a given AI-TST-ME approach and how they affect the predictive capacity across entire mechanisms.

Automated, large-scale data generation enables a feedback loop in which datasets can inform the refinement of a computational approach, which will then produce more accurate datasets. Automated tools have been critical to evaluate thermochemical and rate parameter sensitivity both to the quantum mechanics (QM) methods and to the treatment of various effects (e.g., anharmonic and torsional multidimensionality) in the kinetic model [2,3]. Iterative and systematic improvements will ultimately yield highly-predictive models with well-understood uncertainties. We here discuss one such iteration, investigating the significance of stereochemical effects for *n*-butane oxidation mechanism.

Demonstration

In recent work [4], we used the AutoMech software [5] to construct a reaction network for the first two stages of *n*-butane oxidation. The network additionally included the crucial, radical-generating ketohydroperoxide (and subsequent alkoxy radical) decomposition pathways (see Figure 1). The network was expanded by 20% to include all diastereomeric variants of each species and reaction and AutoMech facilitated computations for the resulting 183 elementary steps. The rate constants were determined with a modest AI-TST-ME approach, which parameterized multi-well multi-channel master equation simulations with CCSD(T)-F12/cc-pVDZ-F12//B2PLYP-D3/cc-pVTZ energies, scaled B2PLYP-D3/cc-pVTZ vibrational frequencies, and a scaled one-dimensional treatment to the rigid rotor partition function. These scaling factors were established during previous benchmarking feedback loops [2].

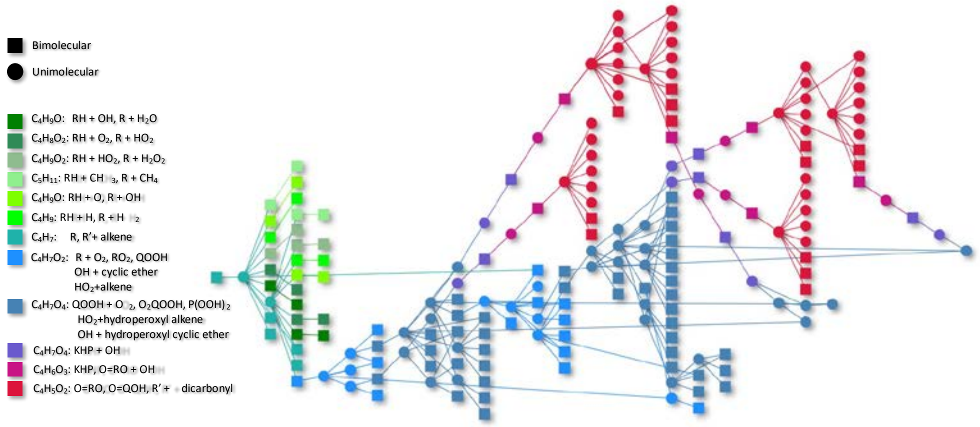

Figure 1. Reaction network for *n*-butane oxidation, where circular nodes represent unimolecular species, square nodes represent bimolecular species, edges represent the reactions between them, and color identifies the stoichiometry.

In this mechanism, stereochemistry influenced both individual rate constants and simulated reaction observables. The 0 K enthalpy differed as much as 7.5 kcal/mol between geometric isomers and their formation barrier heights by as much as 4.4 kcal/mol. Though optical isomers displayed less sensitivity, rate constants with either geometric or optical diastereomerism differed by a median factor of 3.5 at 360 K and 1.6 at 1000 K. Ignition Delay Times (IDT) simulated for the combined *n*-butane and NUIGMech1.1 [6] mechanisms were relatively insensitive to those rate constants which produce geometric or optical isomers. In contrast, the omission of fleeting stereoisomerism (wherein there is fleeting chirality at the reaction site of the transition state) caused deviation in the IDT by nearly a factor of two (see Figure 2a). Accounting for stereochemical effects advances the predictive capacity of *n*-butane oxidation mechanism for IDT simulation but further refinement is necessary for speciation (see Figure 2c).

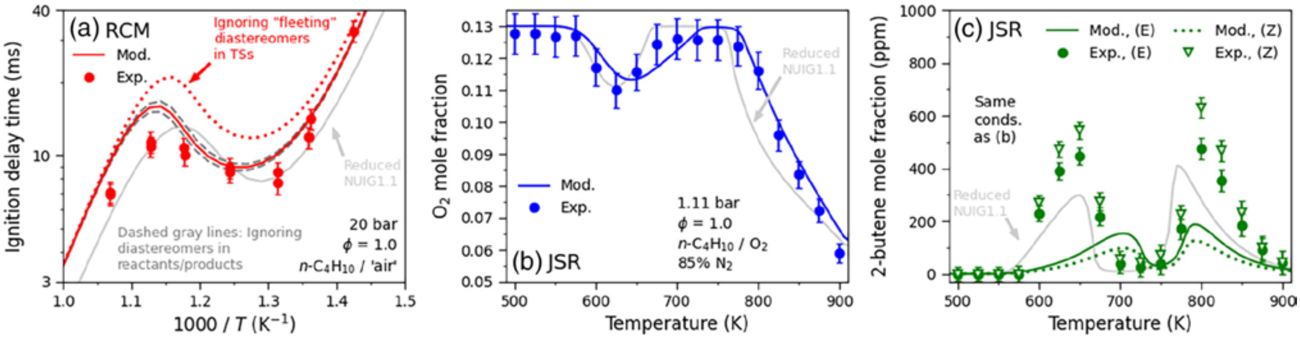

Figure 2. Modeled (lines) and experimental (symbols) values of (a) IDTs in an RCM [7], (b) O_2 concentrations in a JSR [8], and (c) (E)-and (Z)-2-butene concentrations in a JSR [8] during *n*-butane oxidation.

Outlook

Automated software facilitates systematic exploration of the uncertainties built into each computational approach. With stereochemical effects considered, the theory-based *n*-butane oxidation mechanism has considerable predictive capacity. The mechanism can be further refined by utilizing the AutoMech software to improve the QM computations and to further scrutinize the kinetic model (e.g., for non-thermal [9] and variational effects). As the computational approach becomes increasingly reliable, the degree of consumption and secondary reactions that are required to achieve predictive accuracy will need to be evaluated. The results of these benchmarks can guide the construction of other mechanisms. Extending beyond *n*-butane oxidation, however, we anticipate discussion of more complex effects and considerations required for automated software to achieve predictive accuracy for more diverse fuels and conditions.

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Speaker Biography

Sarah Elliott obtained bachelor’s degrees in chemistry and physics from Bethel University in 2015, followed by a PhD in Chemistry from the University of Georgia in 2020 under Prof. Henry F. Schaefer III characterizing electronic structure properties of atmospheric molecules. Having joined in 2020, she currently serves as a Postdoctoral Associate with Dr. Stephen J. Klippenstein, focusing on developing automated workflow tools for large-scale analysis of combustion systems and on thermochemical and kinetic data production with quantified uncertainties and high accessibility. Her interests also extend to the use of machine learning and cheminformatics to enhance data reliability and affordability.

Automatic generation of searchable data archives for reaction model development, benchmarking, and Machine Learning from network exploration tools

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Chemical reaction models can serve to simulate, understand and optimize flames and other chemical processes. For many applications in combustion, large and complex models exist. However, often they are still not complete and therefore do not extrapolate well into conditions for which no experimental validation data exist. The manual completion is tedious and there is no guarantee for completeness. Therefore, software tools are emerging that support this process. They need to automate the routine investigations as much as possible to allow researchers to focus on the scientific tasks. At the same time, they produce huge amounts of data, which they "concentrate" to the desired model. However, all the intermediate geometries, energies, etc. should not be lost because these data can be very useful in future similar work, e.g., to develop machine learning models to speed up the process in the future.

In order for data to be useful, it needs to be findable, accessible, interoperable and reusable (FAIR). This not only includes publishing data with a persistent identifier, such as a DOI, but also includes the use of standard vocabulary, a formally specified language and community standards [1]. In the context of chemical models, the use of standard vocabulary is especially important due to the interdisciplinary nature of that discipline, e.g., the understanding of what a species is may be different for someone who thinks in terms of DFT simulations and atomic structures versus someone who thinks in terms of experimentally accessible observables. Furthermore, being able to identify a species is also useful for linking the model parameters of that species with the data used or generated to obtain these parameters, such as optimized geometries, measured spectra, etc. This parameter provenance information can be valuable for other researchers who want to use the model parameters in their own models and sharing provenance is one aspect of FAIRness [1]. With automated approaches, provenance information could theoretically be provided automatically and in a machine-readable way. However, machine-readability requires a certain standardization and while there are already standard ways to identify molecular structures (e.g., InChIs), the exact level of theory of a quantum chemistry calculation is often provided as human readable string. The latter makes it hard to compare methods automatically, e.g., "B3LYP/6-31G**" and "B3LYP/6-31G(d,p)".

The potential of these automated approaches to evolve into black box methods represents a significant opportunity. However, scientific software is often poorly documented, making it difficult to use or reproduce results, even for people in the same field as the developers. This critique also applies to software produced by our group in the past.

Therefore, comprehensive documentation and compliance with community standards are crucial to fully leverage the data generated by automation tools. Where standards or conventions do not exist, new ones need to be agreed upon.

With the continuing development of our ChemTraYzer (CTY) software, we aim to increase the FAIRness of automatically generated data including intermediate results. CTY can search and find reaction pathways missing in a model, provide high-level rate constants, and is now able to store and archive all relevant model and quantum mechanics data automatically. We are currently developing a new version of CTY that will be released as a beta this spring. The new version will be implemented in Python 3 and entirely modular. The modularity allows for the independent execution of computational chemistry workflows from the molecular dynamics reaction sampling. We implemented a new internal data structure designed with inter-disciplinary and extendibility in mind, e.g., based on IUPAC definition of chemical species [2]. Any computational workflow is directly implemented as a so-called investigation and can be executed by other investigations. This modularity and the underlying data structure in principle also allow other researchers to implement their computational chemistry code using CTY 3 just as a library. Furthermore, we want to enable users to publish the generated "intermediate" quantum chemistry data on special repositories such as iochem-bd [3] or

NOMAD [4], or general purpose ones such as Zenodo [5]. Our plan is to use APIs of such repositories to simplify FAIR data publication.

Since the metadata needed to publish the quantum mechanical data is also provenance data of a final mechanism, it should be possible to supply it as such in the metadata of the chemical model itself. We are currently working on a standard to supply detailed metadata for chemical models. One challenge is here is the need for extendibility to allow different disciplines to add their provenance.

To improve reproducibility of results obtained with CTY version 3 will come with a documentation for users and developers. For this purpose, we use existing software tools such as Sphinx and Gitlab Pipelines. While this requires some time investment in addition to the scientific tasks, we ultimately found these tools relatively easy to use and deem the investment worth the effort. Therefore, we encourage other researchers who have not already published a user documentation, to do so, too.

In summary, we will discuss how open and well documented software, a metadata schema for reaction mechanisms and a simple index on an existing platform (e.g., Zenodo), searchable by species, will allow the community to make their reaction models more findable.

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Automation and Machine Learning in Chemical Kinetics

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Introduction

Due to its complexity, chemical kinetic modeling in combustion for long relied on automation to generate detailed reaction mechanisms [2]. However, the impact of these computerized frameworks is attenuated by the lack of accurate thermodynamic and kinetic parameters for most of the large number of species and reactions predicted to be important. In recent years, machine learning (ML) has permeated chemical kinetic studies [3], offering new ways to accelerate the calculation of elementary rate coefficients, including direct prediction of rate coefficients from the features of the reactants and products, or by using generative neural nets (e.g., [4]) to arrive at saddle point guesses. Here we outline our work on atomistic ML to capture the potential energy surface (PES) at least in the kinetically important regions, and calculate rate coefficients on these surfaces as one would do using DFT or higher-level theories [1].

Automation of quantum chemical methods, another modern approach [5-8] goes hand-in-hand with ML. It has two important roles in this regard. First, automation is indispensable to generate the large amount of kinetic data [9] that is fed into the ML frameworks. Second, the premise of atomistic ML is to provide a very fast potential energy evaluator, which in turn requires algorithms that can similarly rapidly take advantage of ML. In the following we also showcase our recent work using automation for complex multiwell reactions [6, 10].

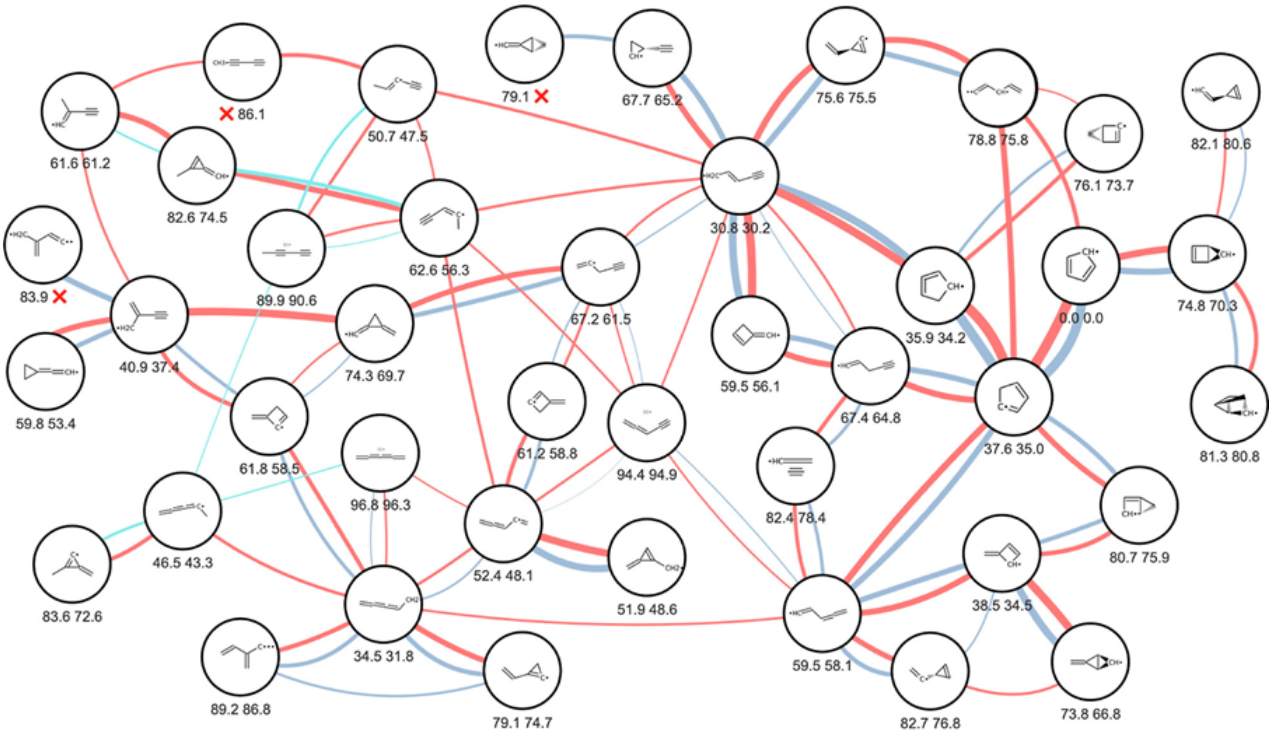

Figure 1. C_5H_5 PES. Blue edges show paths found on the NN PES, while red ones correspond to DFT [1].

General results of automated exploration for C_nH_n, $n = 5–8$ PESs

In recent studies we used our KinBot kinetics workflow [11] (https://github.com/zadorlab/KinBot) to investigate open- and closed-shell systems on C_nH_n, $n = 5–8$ PESs in an automated manner [6, 10, 12]. We showed that we can uncover all previously found pathways and find many new important ones as well. For instance, on the C_7H_7 PES [10] a lower-energy pathway connecting benzyl with vinylcyclopentadienyl, a decomposition mechanism from benzyl that results in side-chain hydrogen atom loss to produce fulvenallene + H, and shorter and lower energy routes to the dimethylene-cyclopentenyl intermediates were found. We also showed that our workflow can assemble the entire master equation for these systems reliably, and thus produce accurate rate coefficients to be used in detailed chemical models. More recently we extended our automated capabilities to couple KinBot to a VRC-TST code [13] to carry out calculations for barrierless reactions as well, which we demonstrate on the reaction of propargyl + cyclopentadienyl → C_8H_8 reaction.

Machine-learning study of C_5H_5 kinetics

In recent work [1] we sampled the KinBot-generated stationary points [6] at the ωB97X-D/6-311++G(d,p) level on the C_5H_5 PES to study the feasibility of a neural network (NN) PES representation to speed up kinetic calculations. We represented structures using atomic environment vectors (AEVs) and the molecular energy was treated as a sum of atomic energies. An ensemble of five NNPESs were trained on energies and forces [14].

We used KinBot to re-explore the C_5H_5 chemistry using the NNPES. As shown in Fig. 1, most of the original (red) pathways were preserved in this attempt (blue). This means that, remarkably, our NNPES combined with our sampling strategy seems to be void of holes or major artifacts in the vicinity of important stationary points, and, therefore, we had no problems navigating this high-dimensional space using KinBot's strategy. We found that while electronic energies at the stationary points are preserved to within a kcal/mol even for transition states, the ZPE-corrected energies, due to relatively larger errors in harmonic frequencies, showed larger discrepancies. The same root cause was identified for the relatively large discrepancies in partition functions at combustion-relevant temperatures between the DFT and NNPES evaluations. Eventually, it led to the degradation of accuracy in rate coefficients when evaluated at the NNPES level as shown in Fig. 2, especially at higher temperatures.

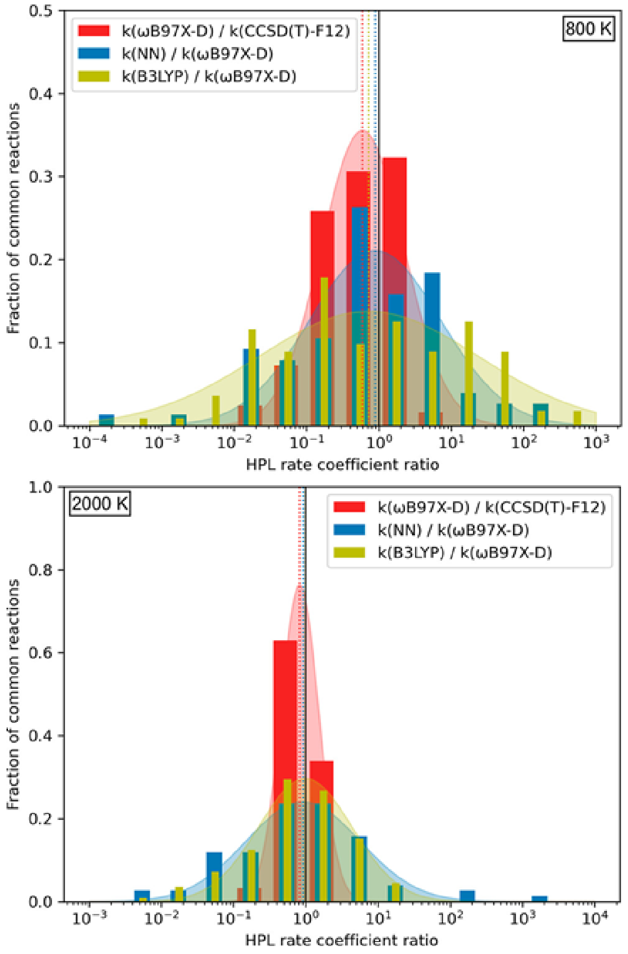

Figure 2. Histogram of the rate coefficient ratio of NN, B3LYP, and ωB97X-D against their reference methods at 800 K (upper panel) and 2000 K (lower panel).[1].

Outlook

A key question for NN-based exploration tools is their extensibility to larger systems and their predictive power for chemical landscapes which they were not trained on. The computational costs of our NNPES are approximately linear in the number of atoms in the system, whereas DFT scales as $O(N^3)$ with the number of electrons, so the speed advantages of the NNPES are evident as the system size grows. The locality of the AEV also means that less training data may be needed for larger systems, as the local environment of atoms within medium sized molecules is often similar to that of larger molecules. We also believe that a more optimized sampling method can decrease the amount of training data and also help improve the model's ability to calculate frequencies. For example, the optimization of minima is typically a simpler task than optimizing transition states; therefore, less training data may be needed in those regions without sacrificing accuracy.

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Speaker Biography

Judit Zádor received her diploma in Chemistry in 2002 and her PhD in Physical Chemistry in 2006 at the Eötvös University in Budapest, Hungary working with Prof. Tamás Turányi on uncertainty quantification of combustion models. She spent the 2001/2002 academic year in the laboratory of Prof. Michael Pilling to work on atmospheric models. In 2006 she conducted experiments as a postdoctoral associate in the laboratory of Dr. Sándor Dóbé in Budapest, and joined Sandia National Laboratories in 2007 working with Drs. James A. Miller and Craig A. Taatjes. Currently she is a Distinguished Member of Technical Staff, working on fundamental aspects of combustion, atmospheric chemistry, and heterogeneous catalysis with emphasis on automation and machine learning. She is a Fellow of the Combustion Institute (2024), received the O. W. Adams Award of the Combustion Research Facility (2020), and is the Project Director of the Exascale Catalytic Chemistry (ECC) project.

Automation in reaction discovery and kinetics

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In recent years, our laboratory has devoted considerable effort to the exploration of potential energy surfaces through automated modelling. This effort has culminated in the development of AutoMeKin.[1]
AutoMeKin stands for *Auto*mated *Me*chanisms and *Kin*etics, and it is an automated protocol to discover chemical reaction mechanisms and simulate the kinetics at the reaction conditions of interest. Although the method was originally designed to find transition states (TSs) from reactive molecular dynamics (MD) simulations, several new tools have been incorporated throughout the past few years.[1] The current pipeline consists of three steps:

1. Exploration of reaction mechanisms through MD simulations or chemical knowledge-based algorithms.
2. Use of Graph Theory algorithms to build the reaction network (RXNet).
3. Kinetics simulations.

The new capabilities include a rare-event acceleration MD algorithm, a new method to explore noncovalently bound structures, heuristics-guided explorations of reaction mechanisms, a new reactive event detection algorithm, statistical analysis of the RXNet, and a web application [3]. Most of these new features belong to the first step of the above pipeline.
The second step consists of the construction of the RXNet. This is initiated with IRC calculations to connect each TS with a reactant/product pair, which are then followed by optimizations of the minima. Finally, all possible connections between every pair of minima are built using the Python package NetworkX.
The networks of chemical reactions can be studied by Graph Theory, where a node corresponds to a minimum while an edge represents a TS connecting two nodes (with or without saddle points). The use of NetworkX also facilitates the study of the structure of the networks by identifying the presence of hubs (highly connected nodes) and providing the shortest paths between reactants and products.
Since the kinetics simulations utilize very simple theoretical methods (such as harmonic TST or RRKM theory), we typically employ AutoMeKin to generate the RXNets. These RXNets are then fed into Pilgrim[2] for computing accurate kinetics.
Finally, our methods enable an efficient construction of reaction networks. However, the obtained RXNets may be very complex, which requires advanced tools to facilitate their visualization and analysis. While experienced users may employ custom scripts to process the computed networks, a more user-friendly approach would facilitate the extension of this kind of automated methods to a larger part of the community.

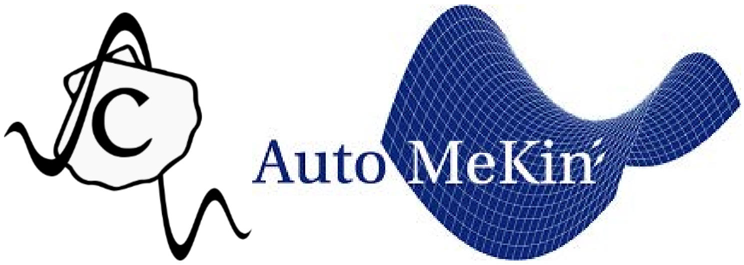

Figure 1: Software developed in our Lab.

In this spirit, the new Python library *amk-tools* [4] has been designed to read and manipulate complex reaction networks, greatly simplifying their overall analysis. The package provides interactive dashboards featuring visualizations of the network, the three-dimensional (3D) molecular structures and vibrational normal modes of all chemical species, and the corresponding energy profiles for selected pathways. Moreover, there is also a growing interest in digital repositories to store and share computational chemistry results, such as ioChem-BD. While the individual calculations could, in principle, be seamlessly uploaded to a database, the picture painted by the (likely abundant) data will not be complete without the underlying network structure. To fill these gaps, we developed the *amk-tools* [4] package, a Python library designed to *parse*, *process*, and *transform* the reaction networks explored by AutoMeKin.

In this talk I will briefly outline the basic theoretical models and present a selection of illustrative examples.

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Speaker Biography

Full Professor at Universidade de Santiago de Compostela (since 2023)
Visiting Professor Université de Lille (2018) and University of Leeds (2013)
PhD at Universidade de Santiago de Compostela, Spain (1995-1999)
My research is focussed on the development of theoretical models to study chemical reactions. Over the last years, I've been involved in the development of AutoMeKin, a computer program for the automated discovery of reaction mechanisms.

Progress in Predicting Reaction Rate Constants: Integrating Molecular Featurization Methods and Machine Learning Models

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Accurate reaction rate constant calculations come at the cost of exploring potential energy surfaces, which quickly becomes prohibitive as the system size grows. This impedes the use of *ab initio* methods for the rapid evaluation of kinetics for large systems or for complex networks of coupled reactions. Recent studies have progressed towards applying and designing machine learning algorithms to predict reaction rate constants or quantities required to compute reaction rate constants. The accuracy of machine learning predictions is heavily dependent on the quality of the data used to train the models. Therefore, one area of interest is to expand the kinetics datasets that have well-determined reaction rate constants, or to generate new kinetics datasets which would enable easy data access, upload and update. Another area of importance is the molecular featurization methods which involve the choice and design of input features and representation. This influences the accuracy of predictions and determines the generalization ability of the model across different chemical systems.

Our recent research focuses on developing an efficient machine learning strategy to predict reaction rate constants with high accuracy. A series of chain alkenes have been selected due to the complexity of molecular structures and the diversity of reaction sites, to study the hydrogen abstraction by OH radical. We initially use conventional molecular structure descriptors along with *ab initio* derived descriptors, i.e., barrier height and bond dissociation energy, to achieve molecular featurization. Non-linear algorithms, including neural networks and kernel methods, are employed to establish the correlation between the input features and reaction rate constants. Our preliminary efforts establish a general machine learning pipeline to accurately predict reaction rate constants tailored to specific reaction type. This approach requires only information on the SMILES[1] representation of the reactant molecular structures and the bond dissociation energy to make accurate predictions over a wide temperature range. Nevertheless, evaluating bond dissociation energies are still time-consuming for large systems even at the DFT level. Also, training models for individual reaction site, which corresponds to a one-to-one mapping, demands substantial time and effort.

Our subsequent efforts aim to circumvent the computational cost and uncertainties by *ab initio* calculations in the molecular featurization process. The new approach adopts an innovative graph embedding generation method to replace the molecular features mentioned above. For the chain alkenes system, a novel set of encoding principles has been devised to capture information regarding reaction sites, isomeric properties, and atomic distribution features. The variant of graph neural networks, GraphSAGE[2], is employed to iteratively enhance the extraction and refinement of graph information, thereby enabling the generation of entire graph embeddings. In comparative analysis of downstream model performance, the feedforward neural network (FNN) model emerges as the best-performing model among those tested. The model's generalization and predictive performance are validated using reactions involving larger chemical systems. The predictions show good accuracy at various reaction sites in two C8 alkene isomers[3, 4], which we select beyond the training datasets. Moreover, the model's generalization capabilities are further evaluated by applying it to a cyclic alkene system, i.e., cyclohexene[5]. The model effectively captures the trends in kinetic behavior and accurately reproduces the results derived from high-precision *ab initio*-TST based master equation calculations within a factor of 1.5, demonstrating its adaptability and effectiveness across varying structural characteristics. The machine learning algorithm devised in the new approach offers a pathway to circumvent the computationally intensive *ab initio* calculations. By simply inputting the SMILES representation of products and the numerical identifier for each reaction site, we can rapidly obtain reaction rate constants over a wide temperature range. Also, attributed to the excellent ability to discern molecular structures by graph neural networks, our method exhibits good transferability, offering multiple ways to train machine learning models. For example, we can design unique encoding principles to train models for various reaction systems, with species from either the same category or different categories and reactions of either a single type or multiple types, by using a universal encoding rule to generate robust models.

In future research endeavors, our focus will progress towards creating a shared online platform for predictions of reaction rate constants and quantities needed to obtain rate constants, by using the machine learning strategy we propose. This platform will offer intuitive user interfaces for various chemical systems, including alkanes, alkenes, aromatic hydrocarbons and other complex compounds. Before that, we should generate kinetics datasets from advanced theoretical calculations or reliable experimental measurements. These data will be instrumental in enhancing the robustness and accuracy of machine learning models, thereby laying the groundwork for large scale exploration within the realm of machine learning kinetics.

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Speaker Biography

Since 2020: Associate Professor at Dalian University of Technology, China
2018-2019: Assitant Professor at Dalian Maritime University, China
2015-2018: Post Doc at the Shanghai Jiao Tong University, China with Prof. Fei Qi
2013-2014: Joint PhD at Argonne National Laboratory, USA with Dr. Stephen J. Klippenstein
2009-2015: PhD in combustion chemistry, University of Science and Technology of China
2005-2009: Bachelor of applied physics, China University of Petroleum (East China)

Topic 5. Chemical Kinetics Mechanisms: Progress in accuracy and details.

Keynote presentation

Progress in Chemical Kinetics Modeling through the Prism of Synchrotron-Based Photoelectron Spectroscopy

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Recent advances in elementary-step-based kinetic modeling have significantly enhanced its predictive capabilities due to improvements in combustion analysis tools, theoretical calculations, and computer science. Modern models effectively incorporate the complex chemistry of various fuels into large-scale simulations, aligning quantitatively with experimental data like ignition delay times and flame speeds, and mole fraction species profiles under various conditions. However, accurately predicting combustion characteristics of novel oxygen- and nitrogen-rich fuels remains challenging due to missing critical species and key reactions or inaccuracies in kinetic parameters, reflecting a need for more focused theoretical and experimental research.

Addressing these challenges requires a mix of theoretical calculations and laboratory combustion experiments. Kinetic models can be developed using molecular-level data derived from electronic structure, ab-initio methods, and statistical theory by providing required thermochemical and kinetic parameters for species and related elementary reactions[1,2]. The resulting predictions of the kinetic models can then be validated against combustion data from various experimental setups, both time-dependent and steady state, like homogeneous flow reactors, laboratory flames, rapid compression machines, and shock tubes operating under engine-relevant conditions. These setups employ a range of analytical techniques including spectroscopy, mass spectrometry, and chromatography to identify and quantify products, including intermediates, measure rate coefficients with their temperature/pressure dependencies, and product branching fractions.

Among these methods, synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) has proven to be efficient for detecting and quantifying intermediates in combustion systems[3–7]. It uniquely combines a tunable light source with mass spectrometry for sensitive, multiplexed measurements. One of the advantages, is that it offers a unique benefit in differentiating isomers through analyzing mass-selected photoionization efficiency (ms-PIE) curves that are uniquely determined by the vibronic structure of molecules.

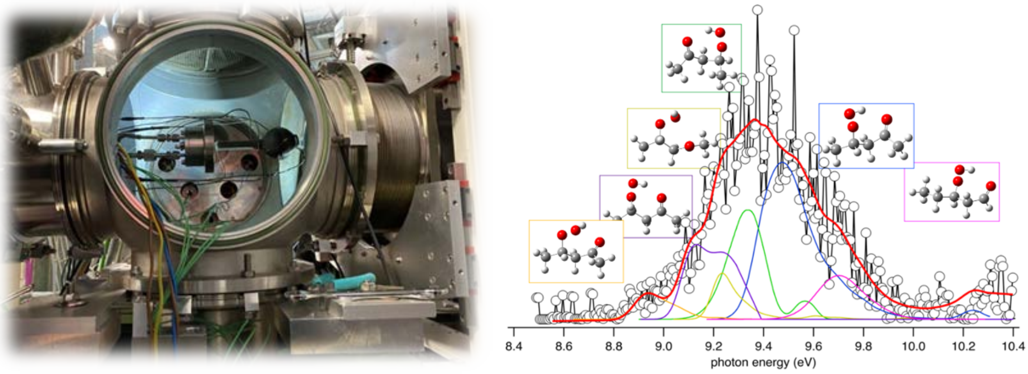

Figure 1. (left) Photo of the experimental setup showing a jet-stirred reactor mounted in the SAPHIR vacuum chamber connected to the DELICIOUSIII PEPICO spectrometer on the VUV DESIRS beamline of the Soleil synchrotron; (right) experimental photoelectron spectrum of m/z 118 recorded during the oxidation of n-pentane at 585 K compared to simulated photoelectron spectra of ketohydroperoxide conformers and isomers.

However, distinguishing several isomers with close ionization energies remains challenging, which has led within the last decade to an increasing use of SVUV-PEPICO, a photoelectron spectroscopy technique, providing a higher degree of isomeric discrimination by analyzing the photoelectron kinetic energy alongside the corresponding ion. Its photoelectron spectrum (PES) offers improved sensitivity and selectivity, with distinct peaks representing transitions from the fundamental electronic level[8,9].

The application of SVUV-PEPICO for combustion studies, with pioneering work on flames[10,11] has been also applied recently to oxidation experiments in flow reactors (see Figure 1)[12]. This keynote will focus on the latest advances and achievements made for kinetic modeling in oxidation chemistry (see Figure 2) using the PEPICO spectrometer on the VUV DESIRS beamline of the Synchrotron SOLEIL in France. It will conclude by highlighting ongoing challenges in mass resolution, sensitivity, species quantification, especially isomers, and their impact on the predictive accuracy of kinetic models.

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Speaker Biography

Jérémy Bourgalais earned his PhD in Physics in 2016 from the University of Rennes, France, where he conducted his research at the *Institute of Physics of Rennes* (IPR). Following this, he completed postdoctoral work at the NOAA *Earth System Research Laboratory* in Boulder, Colorado, USA, working with Dr. James B. Burkholder, and at the *Atmospheres and Spatial Observations Laboratory* (LATMOS) near Paris, working with Prof. Nathalie Carrasco. In 2020, he joined *the Reactions and Chemical Engineering Laboratory* (LRGP) in Nancy, France, as a full-time permanent CNRS associate scientist.

His research interest focuses on fundamental molecular physics and gas-phase physical chemistry, aiming to understand the chemical evolution of real-world reactive diluted environments, such as planetary atmospheres and industrial processes. His work involves laboratory experiments that integrate gas flow reactors with advanced analytical techniques in optical spectroscopy and mass spectrometry. These experiments employ various types of photon energy sources, such as synchrotron radiation, lasers, and plasma, to explore the molecular dynamics and chemical kinetics in isolated and surrounded molecular systems. By coupling these experimental investigations with theoretical quantum calculations, he contributes to the development of predictive chemical kinetic models. These models are crucial for understanding the formation of tropospheric aerosols and the emission of pollutants by new energy carriers like biofuels.

Invited presentations

Resonance Stabilized Radical Formation by Reactions of OH with Conjugated Hydrocarbons

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Resonance stabilized radicals (RSRs) play an important role in combustion flames, from the formation of the first aromatic rings [1] to the clustering of large soot precursors.[2] They are formed in flames by direct pyrolysis or through bimolecular reactions between radicals, such as the OH radical reactions with conjugated hydrocarbons.

At low and intermediate temperatures, OH reactions with unsaturated hydrocarbons proceeds through the barrierless formation of a van der Waals (vdW) complex between the OH radical and the molecule's p system. The radical can then bond to one of the double-bonded carbon atoms through an energy barrier slightly above that of the vdW complex. In the case of OH addition onto a conjugated double bond, the resulting reaction adduct is often stabilized by resonance and accumulates in the gas phase. At higher temperatures, the weakly bonded vdW complex rapidly dissociates back to the reactants making H-abstraction the dominant channel, forming a hydrocarbon radical (which may itself be resonance-stabilized) and a water molecule. Similarly, reactions of OH with conjugated α,β-unsaturated carbonyl compounds mostly lead to the formation of RSRs, both through addition and abstraction mechanisms. If the resulting unpaired electron is in a-position from the carbonyl group, the radical product becomes a substituted vinoxy radical. Such radicals are predicted to have a lower reactivity toward molecular oxygen, [3] mostly due to a competitive back dissociation.

The competition between the addition and abstraction mechanisms leads to a rate coefficient that decreases with increasing temperature to a minimum value before increasing at higher temperatures.[4] Figure 2 displays the Arrhenius plots for reactions of the OH radical with cyclopentenone, substituted cyclopentenone, and cyclopentanone. At room temperature, association of OH onto the double carbon bond of 2-cyclopenten-1-one is found to be a competitive entrance pathway. The kinetic measurements suggest that the addition pathway may accounts for up to 75% of the overall reaction products at 300 K while abstraction dominates at 500 K. RRKM–ME calculations and isomer sensitive product detection suggest that the vinoxy-like radical is the main association product, with minimum contribution from addition of the OH to the b-position.

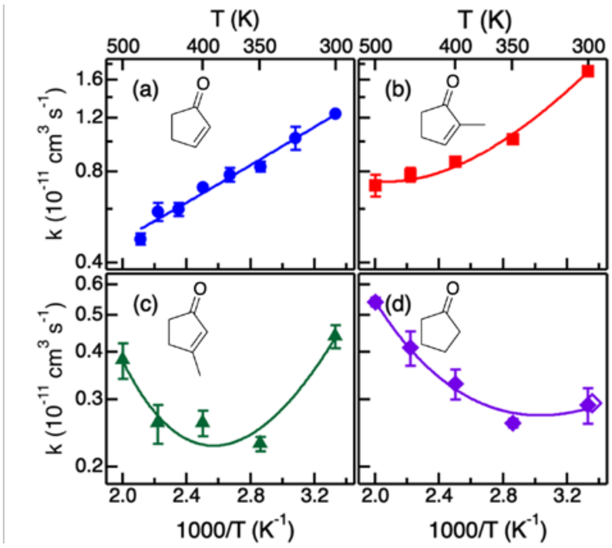

Figure 1. Arrhenius plots for reactions of the OH radical with (a) cyclopentenone, (b) 2-methyl-cycplopentenone, (c) 3-methyl-cycplopentenone, and (d) cyclopentanone at 4 Torr.

The detection of resonance stabilized radicals from OH reactions using VUV soft ionization is facilitated by their low ionization energy and long reaction lifetime. Figure 2 displays the photoion spectrum of m/z 81 (black markers) obtained upon 248-nm irradiation of a mixture containing H_2O_2 and 2-cyclopenten-1-one at 8 Torr and 600 K. The ion onsets match the calculated adiabatic ionization energy of two resonance stabilized radicals. The simulated photoion spectrum of these radicals are fitted to the experimental spectra.

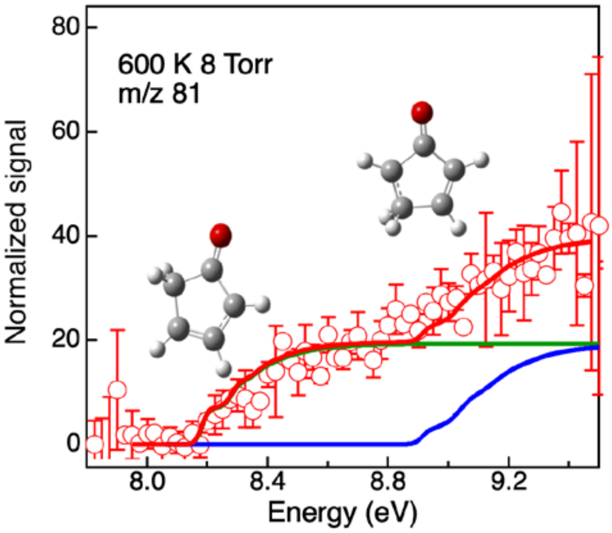

Figure 2. Photoion spectrum of m/z 81 (black markers) from the OH + 2-cyclopenten-1-one reaction together with the integrated Franck-Condon factors if the abstraction isomers(red line)[5].

The reaction of the OH with cyclopentadiene has also been shown to form RSRs over the 300–1000 K temperature range.[5] Below 500 K, addition is the main reaction pathway, leading to the formation of the resonance-stabilized 5-hydroxycyclopent-2-en-1-yl. The non-resonance stabilized isomer is not detected. At higher temperature, the dominant reaction pathway is abstraction of a hydrogen from the sp^3 carbon leading to the formation of the RSR cyclopentadienyl.

Overall, the products from the reaction of the OH radical with cyclic conjugated hydrocarbons and ketones are expected to be RSRs over a very wide range of temperature, formed through abstraction and addition mechanisms. These radicals are likely to accumulate in flames and contribute to molecular growth schemes through reaction with abundant hydrocarbons and self-reactions.

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Speaker Biography

Dr. Fabien Goulay is an Associate Professor in the Department of Chemistry at West Virginia University in Morgantown, WV. He received a PhD in physics from the University of Rennes (France) under the direction of Dr. Bertrand Rowe and continued as a postdoctoral fellow first in the group of Prof. Stephen Leone at UC Berkeley and then with Dr Hope A. Michelsen at Sandia National Laboratories. He was an associate specialist at UC Berkeley, working at the Lawrence Berkeley Lab before starting his carrier at WVU. Goulay’s research focuses on the experimental investigation of elementary radical processes in the gas phase and at the surface of nanoparticles.

Accurate kinetics calculations for peroxy radical reactions

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Peroxy radicals ($RO_2\cdot$) are the central reactive intermediates of oxidation reactions formed by rapid addition of oxygen molecules to initially generated radicals of organic fuels in low-temperature combustion or of volatile organic compounds (VOCs) in atmospheric chemistry. In the past decades, extensive theoretical studies have devoted to obtaining accurate kinetics of key peroxy radical reactions and revealing the role of isomerization reactions of peroxy radicals via intramolecular hydrogen transfer ($RO_2\cdot$ to ·QOOH) in the radical chain branching in the autoignition and in oxidation mechanism of VOCs. However, there exist a few challenges in accurate kinetics calculations for peroxy radical reactions. First, some key species in peroxy radical reactions may have inherent multireference characters, rendering the failing of single-reference-based electronic structure methods for potential energy surfaces (PESs) calculations and raising the requirement for expensive multi-reference methods. Second, the anharmonicity of potential energy surface may have a particularly significant effect on kinetics of complex peroxy radical reaction systems. For example, in the H-shift reactions of $RO_2\cdot$ to ·QOOH, both the reactants $RO_2\cdot$ and products ·QOOH with multiple rotational single bonds have a much larger number of distinguishable conformers and thereby a more remarkably multi-structural torsional anharmonicity than the cyclic transition state in which the internal rotations are restricted by the ring structure. Thus, the kinetics calculations must take into account this multi-structural torsional anharmonicity. Furthermore, the tunneling and pressure may have a nonnegligible influence on the kinetics, and they need additional attention.

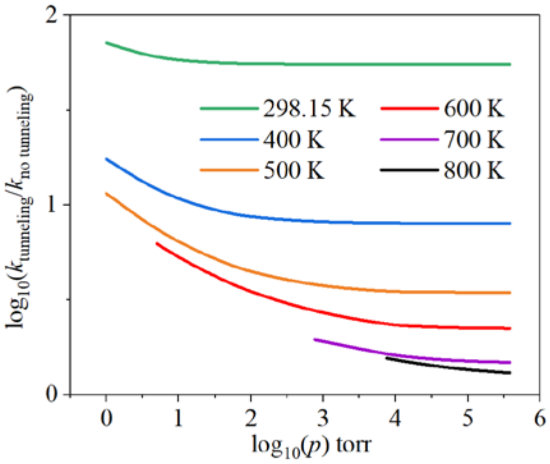

Figure 1. The pressure dependent tunneling effect on the phenomenological rate constants of H-shift reaction of Z-δ-ISOPOO [1].

In our recent theoretical study [1] on the Z-δ-(4-OH, 1-OO)-ISOPOO radical chemistry, we have detailedly discussed the challenges mentioned above. Z-δ-(4-OH, 1-OO)-ISOPOO radical is a very key species in the OH radical recycling mechanism in isoprene oxidation. With the full consideration of accumulation and consumption channels of Z-δ-(4-OH, 1-OO)-ISOPOO radical, we studied and discussed its fate over a wide temperature and pressure range by solving the energy-resolved master equation (ME). The ME calculations are based on a high-precision PES obtained by a composite method WMS which were specially designed for the systems with multireference characters. Both multi-structural torsional anharmonicity and tunneling are demonstrated to be important for accurately calculating kinetics of the studied system. We observed non-negligible pressure dependence of the fate of Z-δ-(4-OH, 1-OO)-ISOPOO radical at combustion temperatures (up to two orders of magnitude). More interestingly, we found pressure-dependent tunneling effect on the phenomenological rate constants of the H-shift reaction channel as a result of the competition with the O_2 loss reaction. (See Figure 1)

We further carried out a comprehensive theoretical study [2] on four typical intramolecular hydrogen shift reactions of peroxy radicals ($RO_2\cdot$, R = ethyl, vinyl, formyl methyl, and acetyl, see Figure 2) by evaluating their multireference character, recommending model chemistry, and calculating the kinetics based on a full consideration. We found that a mild-to-moderate multi-reference character of PES is widely present in the four reactions by a comprehensive assessment of the T_1 diagnostic, the %TAE diagnostic, the M diagnostic, and the contribution of the dominant configuration of the reference CASSCF wavefunction (C_0^2). We investigated the effect of multi-reference characters on electronic structure calculations by comparing the PESs of the four reactions calculated by the multi-reference method CASPT2 in the complete basis set (CBS) limit, the single-reference method CCSD(T)-F12, and the WMS method. We obtained averaged mean unsigned deviations (MUD) up to 1.72 kcal/mol of CCSD(T)-F12 from the benchmarked results when ignoring the multi-reference character. Further tests for single-reference Kohn−Sham (KS) density functional theory methods gave even larger deviations. Therefore, we specifically fitted a new hybrid-meta GGA functional (M06-HS) for the four typical H-shift reactions of peroxy radicals based on the accurate benchmarked values. The M06-HS method decreases the averaged MUD to 0.34 kcal/mol over five tested basis sets, being the best in the tested 38 KS functionals.

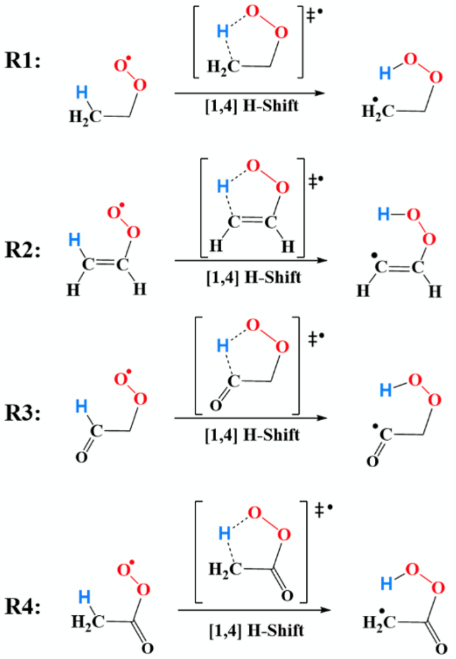

Figure 2. Four typical peroxy radical intramolecular hydrogen shift reactions [3].

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Speaker Biography

Xuefei Xu is an associate professor of the Center for Combustion Energy and the Department of Energy and Power Engineering at Tsinghua University in China. She received her Ph.D. in Physical Chemistry from Xiamen University in China in 2006 and was a lecturer of the Department of Chemistry at Xiamen University in 2006-2008. She was a postdoctoral associate with Professor Yehuda Haas at the Hebrew University of Jerusalem in 2008-2010 and with Professor Don Truhlar at the University of Minnesota in 2010-2015. Her research interests focus on theoretical and computational study of chemical reaction kinetics, nonadiabatic dynamics simulation, and catalysis.

Detailed, time-resolved experimental quantification of reaction intermediates: challenges and opportunities for mechanism development.

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Combustion involves extensive systems of coupled pressure- and temperature-dependent reactions that interact with heat and mass transport in very complex environments. Chemical mechanisms that describe fuel combustion often consist of thousands of species and tens of thousands of reactions, with many estimated and highly uncertain rate parameters. From the experimental point of view, quantitative time-resolved speciation measurements have the highest potential to discover chemical pathways, determine reaction rate coefficients, and validate complex mechanisms. However, measurements of reactive species are difficult because they are short-lived and occur in low concentrations. This challenge is exacerbated for multi-channel reactions, in which different isomers of primary or secondary intermediates may have markedly different reactivity.

One promising approach to address this challenge was recently developed at Sandia National Laboratories by coupling a high-pressure flash photolysis reactor with time-resolved, multiplexed, synchrotron-based tunable vacuum UV photoionization mass spectrometry (SVUV-PIMS) detection. SVUV-PIMS is a sensitive, universal probe method that distinguishes among chemical isomers with the same sum chemical formula using their distinct photoionization (PI) spectra and mass fragmentation patterns. It has been successfully used with jet-stirred reactors to detect key combustion species like ketohydroperoxides, alongside unsaturated hydrocarbons, carbonyls, ethers, small molecules (e.g., CO, CO_2, H_2O), and others.

The Sandia high-pressure PIMS apparatus [1] uses pulsed laser photolysis of radical precursors to start chemistry in dilute gas mixtures in a 0-D, constant-*T*, constant-*P* reactor. Following photolysis, reaction progress is probed in real-time and coupled reaction pathways can be unraveled from the formation and decay timescales of the detected species. Another important capability of our apparatus is in detecting radicals and other reactive compounds. Gas is sampled out of the reactor without wall contact and expanded into a vacuum chamber, preserving unstable species. It is then ionized and detected with ~25 µs time resolution by a uniquely sensitive mass spectrometer, utilizing a novel "high-density" ionization scheme.

The key feature of our approach is that it uses simplified reaction conditions to enable quantitative, simultaneous, time-resolved measurements of many products and intermediates to maximally constrain chemical mechanisms. Dilute gas mixtures with fuel concentrations of $<10^{15}$ cm^{-3} and radical concentrations $<10^{13}$ cm^{-3} suppress secondary chemistry and accentuate primary reactions of interest. Furthermore, experiments can be tuned to focus on specific reaction classes: for example, peroxy radical (ROO) reactivity can be probed below typical combustion temperatures, where the number of reaction channels is reduced.

We have recently demonstrated this approach in oxidation studies of several model compounds: dimethyl ether (DME), [2] diethyl ether (DEE), [3] tetrahydrofuran (THF), [4] and cyclopentane (CP). [5] In each case, we produced fuel radicals (R·) by photolytically generated Cl-atom H abstraction at *T* up to ~700 K and *P* up to 10 bar. We detected the primary peroxy radicals (ROO·), decomposition products following ROO· ↔ ·QOOH isomerization, ·OOQOOH radicals from $\cdot QOOH + O_2$, and hydroperoxides produced from ·OOQOOH. Nearly all intermediates we detected have not been observed before, and Figure 1 shows three representative examples of reaction intermediates we characterized by SVUV-PIMS.

Most importantly, our approach enables the quantification of species, for which authentic reference PI spectra cannot be obtained, such as those in Fig. 1, from a global C atom balance analysis. Specifically, the ion signals in PIMS experiments must be scaled by PI cross-sections to obtain absolute concentrations. Since the species we detect have distinct time evolution and *T*-dependence, their unknown PI cross-section can be fitted such that the sum C atom content of all products and intermediates matches that of the depleted fuel compound at all kinetic times and all *T* simultaneously, thus determining their concentrations directly from experiment. Figure 2 illustrates this approach for the case of CP oxidation. [5] Fig. 2 (top) shows the dominant reaction sequence (with detected species highlighted), at 450 – 650 K. Fig. 2 (bottom) presents the depleted CP and the quantified intermediates at 550 K, determined *via* a global C balance fit to all data at 450 – 650 K.

The experimental advances such as described above are enabling a new generation of chemical mechanism development and validation studies, anchored by time-resolved, isomer-specific quantification of reactive species at the heart of complex reaction networks. These new data require models to predict not only the time-averaged product yields, but also the formation and decay timescales of radicals, unstable closed-shell species, and long-time products.

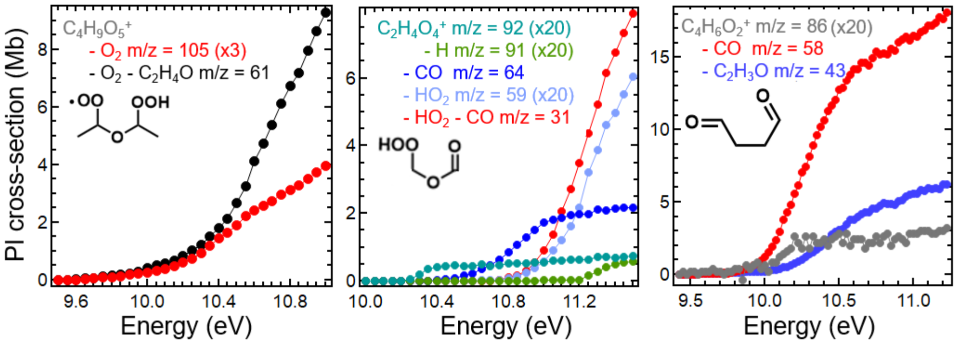

Figure 1. Absolute PI spectra (parent and/or largest fragment ions) of representative intermediates in ether oxidation reactions. *Left:* the dominant ·OOQOOH isomer in DEE oxidation; *Middle*: the main ketohydroperoxide species in DME oxidation; *Right*: the dominant species formed by unimolecular decomposition of ·QOOH in THF oxidation.

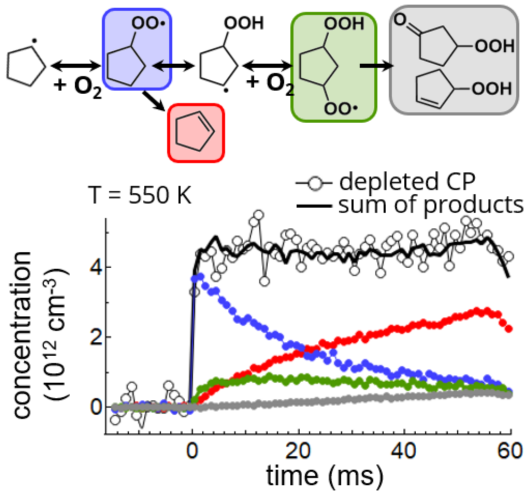

Figure 2. Top: the dominant reactions in our CP experiments at 10 bar and 450 – 650 K. Bottom: Absolute concentrations from a global C balance fit. Color symbols correspond to products, marked by color boxes above. White circles show the concentration of CP, depleted after photolysis; solid black line is the sum of all detected products

Comparisons of our data to literature models revealed large discrepancies in all studied fuels: DME, DEE, THF, and CP. One common feature of these gaps is the overprediction of fuel consumption and of hydroperoxide production at all temperatures we surveyed. Initial tests suggest that this behavior is sensitive to the competition of ·QOOH decomposition vs. ·QOOH + O_2 reaction and to the branching of ·OOQOOH decomposition into ketohydroperoxides + OH vs. unsaturated hydroperoxides + HO_2. [6] Evidently, the rate coefficients for these key pathways in low-*T* oxidation reactions may not be properly represented in the prevailing literature mechanisms, and indeed some relevant reaction channels may be missing entirely. For example, we see that for cyclic molecules CP and THF unsaturated hydroperoxides are formed in significant yields from ·OOQOOH, yet these pathways are often excluded from combustion mechanisms.

In the future, we envision synergistic strategies in which 1) sensitivity analyses of available mechanisms find experimental conditions where certain reaction classes can be optimally constrained, 2) experiments provide highly detailed, time-resolved quantification of key intermediates and products, 3) quantum chemical calculations yield theory-based starting guesses for key rate parameters, and 4) advanced modeling optimizes mechanisms within theory-informed uncertainty bounds. These strategies would greatly benefit from developments in modeling, uncertainty quantification, and optimization methods, possibly involving genetic algorithms, machine learning, and other advanced computational approaches.

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Speaker Biography

Leonid Sheps is an experimental physical chemist with interests in molecular spectroscopy, photochemistry, and chemical kinetics. He obtained his PhD from the University of Wisconsin, Madison (USA) and had a postdoctoral appointment at JILA, at the University of Colorado, Boulder (USA). He is currently a staff scientist at Sandia National Lab in Livermore, CA (USA). His research focuses on gas-phase and plasma reaction networks and on the development of optical and mass spectrometry instruments and techniques.

Uncertainties of Thermochemistry and their Implementation in Kinetic Models

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Over the past decades, kinetic modeling has greatly advanced by following a successful tradition of tackling the least certain parameters of detailed chemical kinetic models. Obtaining "chemically" accurate activation energies has been a major obstacle in the past, yet state of the art methods achieve uncertainties below 1 kcal/mol for about a decade by now [1]. With this major obstacle practically out of the way, research attention shifted to reaction entropies and to thermodynamic properties of reactants, intermediates, and products of the chemical reactions. For a long time, thermodynamic properties have been mostly obtained via group additivity methodologies (GAMs), yet the increase in available computational power and progress in automated computational chemistry [2] greatly enhances the quantum mechanics (QM)-based dataset of thermodynamic properties. In this work, three questions and issues regarding thermodynamic properties will be discussed in the context of detailed chemical kinetic models:

First, the uncertainties associated with QM-based thermodynamic properties are often difficult to fully quantify. While standard enthalpies of formation are generally well-studied in terms of uncertainties [3], the uncertainties associated with the standard entropy and the heat capacity are less well-studied.

Second, even if highly accurate thermodynamic properties are available, inaccurate fitting for producing NASA parameters or naming and duplicate issues arising when combining different mechanisms introduce additional uncertainties in the kinetic model.

Third, intermediates of pressure-dependent reactions come with stationary non-Boltzmann energy distributions which directly impact the partition function of these molecules and therefore their thermodynamic properties.

Since pressure-dependent reactions are typically defined in one direction in kinetic models, the reverse reaction is obtained through chemical equilibrium assumptions, using the equilibrium thermodynamic properties. This introduces additional uncertainties in the kinetic model.

To address the first issue, thermodynamic properties obtained in prior studies by the author for a series of compounds relevant for 2-methoxy-1,3-dioxolane, n-pentane, nitrosopentane, nitropentane, amylnitrite, amylnitrate, n-pentanol, methoxy pentane, methyl tert-butyl ether, n-butane, 2,2-dimethoxypropane, methoxy methanol, cyclopentane, ethyl formate, all methyl, dimethyl, and ethyl 1,3-dioxolane isomers, diethyl carbonate, vinyl acetate, trimethoxy methane, bis(methoxymethyl)ether, ethyl acetate, and 2-butanol have been used for checking the quality of state of the art thermodynamic property calculations. All these computations are based on the B3LYP-D3BJ/def2-TZVP level of theory for molecular structures, harmonic oscillators, and one-dimensional hindered rotors and standard enthalpies of formation were obtained using the atomization approach at the G4 level of theory. For the latter, Somers and Simmie reported a mean unsigned error (MUE) of 0.4 kcal/mol, well below the 1 kcal/mol threshold for chemical accuracy [3]. A total of 285 species are included in the dataset and these have been compared to GAM-based thermodynamic properties [4], both of which are validated against literature standard enthalpies of formation $\Delta_f H^0$, standard entropies S^0, and heat capacities c_p for 25 species. Figure shows this comparison, aiming at consolidated uncertainties for $\Delta_f H^0$ and c_p which can be used in kinetic models for testing sensitivities to thermodynamic properties.

The complete comparison between QM and GAM shows that GAM deviates from the QM results on average by 2.8 kcal/mol for the standard enthalpies of formation and by 1.3 R for standard entropies and heat capacities, with R being the ideal gas constant (cf. left parts in Figure). In the classical limit, the heat capacity of a harmonic oscillator equals R, meaning that a deviation of 1.3 R represents a maltreatment of 1.3 internal degrees of freedom on average. Since the total dataset includes a significant number of radicals (highlighted in light red in Figure), comparison to the literature for stable compounds expectedly yields smaller uncertainties (cf. right parts of Figure). One can conclude that state of the art QM-based thermodata comes with uncertainties of 1.2 kcal/mol for standard enthalpies of formation and only 0.2 R for combined standard entropies and heat capacities. GAM is often similarly accurate, yet can occasionally produce highly uncertain results, accumulating in the larger MUEs for the GAM approach.

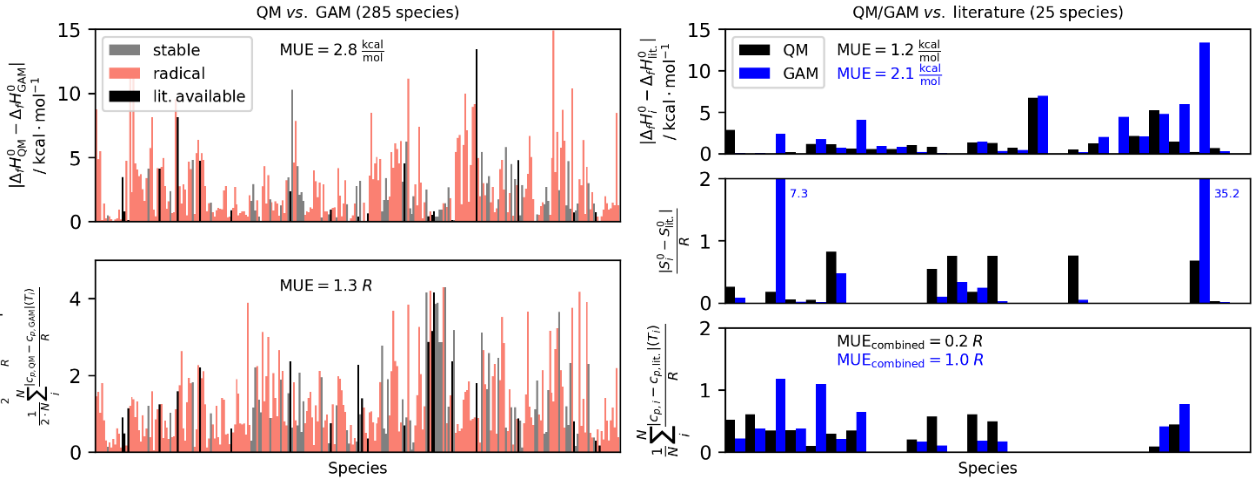

Figure 1. Comparison of QM- and GAM-based thermodynamic properties to each other (left) and to literature data (right).

To address the second issue, state of the art mechanisms have been analyzed in terms of their consistency of thermodynamic properties and representations of these properties. Systematic analysis of NASA parameters revealed inconsistencies, mainly stemming from the limited temperature range used to fit thermodynamic properties. Classically, heat capacity data used to obtain NASA parameters were provided for temperatures ranging from 300 to 1500 K, yet ignition events and flame chemistry typically involve much higher temperatures. Since the polynomials used to represent the thermodynamic properties misbehave outside their fitting range, severe uncertainties can be introduced. This problem can be solved by refitting the thermodynamic properties and imposing the correct limiting behavior, namely the low and high temperature limits. Moreover, the same species might come with multiple definitions when combining different kinetic models for describing, e.g., fuel blend chemistry. Each definition fits into the respective original mechanism and dropping one or the other introduces uncertainties in the combined model, as only one sub-mechanism sustains the correct thermodynamic properties for calculation of, e.g., reverse reaction rate coefficients.

To address the third issue, pressure-dependent reactions have been investigated, the reverse reactions of which have either been calculated through the typical equilibrium assumption, i.e., through the thermodynamic properties of the reactants and products, or through the underlying chemical master equation (ME) simulations. In the latter case, the forward and backward reaction rate coefficients correctly account for the stationary non-Boltzmann energy distributions of the involved species. When using the typical equilibrium-based approach, the reverse reaction rate coefficients differ from those obtained through the more accurate ME simulations, introducing additional uncertainties in the kinetic model.

To conclude, uncertainties associated with thermodynamic properties became increasingly relevant due to the reduction of uncertainties associated with parameters, such as the activation energy. State of the art methods provide near chemical accuracy thermodynamic properties, with standard enthalpy of formation uncertainties of about 0.4 to 1.2 kcal/mol and combined standard entropy and heat capacities uncertainties of roughly 0.2 to 1 R. Additional uncertainties, however, arise from potentially inaccurate implementation of these thermodynamic properties in kinetic models. Insufficiently large temperature ranges for fitting or the omission of the correct limiting behavior of thermodynamic properties could lead to severe deviations due to the polynomic nature of the NASA format. In addition, the commonly used equilibrium-based computations of reverse reaction rate coefficients introduce deviations from to the actual reverse reaction rate coefficients. With the discussion of the presented three issues, the author hopes to aid the development of more accurate detailed chemical kinetic models and help avoiding unnecessary uncertainties.

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Speaker Biography

Malte Döntgen studied mechanical engineering at RWTH Aachen University, Germany, and obtained a PhD in the group of Prof. Dr. Kai Leonhard on reactive molecular dynamics simulation and theoretical kinetics at the same university. During his PhD, he visited Dr. Stephen Klippenstein at the Argonne National Laboratory, where he studied pressure-dependent and non-Boltzmann chemistry. After his PhD, he worked as a postdoctoral researcher in the group of Dr. Arkke Eskola at the University of Helsinki, Finland, on oxidation of resonance-stabilized radicals. Afterwards, he worked as Feodor Lynen Fellow in the group of Prof. Dr. C. Franklin Goldsmith at Brown University, Rhode Island, United States, on fuel pyrolysis using combined ab initio and laser schlieren methodologies. Then he returned to RWTH Aachen University as postdoctoral research fellow in the group of Prof. Dr. Karl Alexander Heufer. At RWTH he extended his research focus to shock tube and rapid compression machine ignition and laser experiments. Currently, he is working as a Chief Engineer at the Chair of High Pressure Gas Dynamics of Prof. Heufer, leading the institute’s quantum chemistry research. His current research interest are non-Boltzmann dynamics in chemical and gas dynamic systems.

Surrogate model development: a focus on the interaction chemistry

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There is an increasing demand for kinetic models of surrogate components to predict the combustion and emissions of real fuels. C3MechV3.3 is developed by the Computational Chemistry Consortium (C3) with detailed chemistry for important surrogate fuel components as well as NOx and PAHs [1].

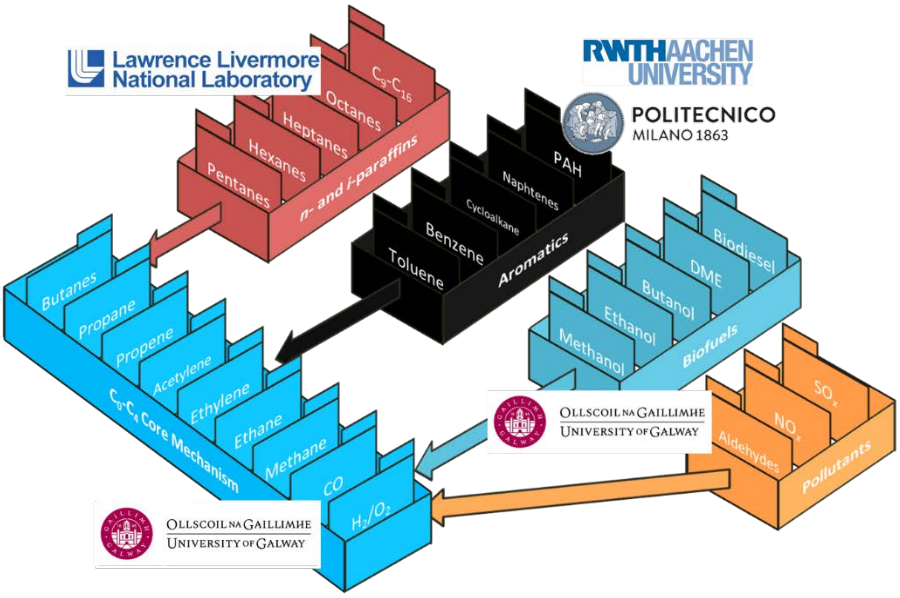

Figure 1. Illustration of component library and of C3Mech modular structure [1].

This presentation will give a brief introduction of C3MechV3.3, including the mechanism structure and major associated challenges in development. Moreover, since some advanced engine combustion strategies are based on binary fuels like natural gas/diesel, alcohols/diesel, alcohols/gasoline, ammonia/diesel, etc, it is also necessary to ensure the surrogate model is reliable in predicting the fuel reactivity of these binary fuels. This will need a particular focus on the interaction chemistry between the surrogate components.

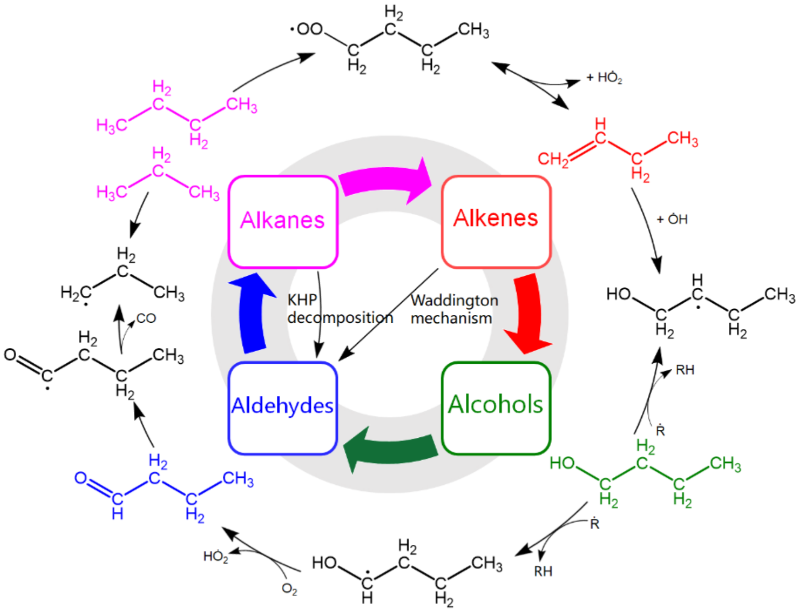

Figure 2. Interdependence of alkanes, alkenes, alcohols and aldehydes.

In general, the interactions occur via the radical pool, while some interaction reactions via fuel radicals can also be important depending on the fuel blends. Thus, a discussion on the interdependence of alkanes/alkenes/alcohols/aldehydes, the interaction chemistry between ammonia/*n*-heptane [2], and the interaction chemistry between NOx/TPRF will be given to highlight the importance.

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Speaker Biography

Dr Shijun Dong is currently a lecturer at Huazhong University of Science and Technology (HUST) in China. His research interest includes combustion chemistry and engine combustion. He received his PhD degree in 2018 from HUST in engine combustion and emission control. Afterwards, he worked as a post-doctoral researcher in combustion modelling from 2018 to 2021 at C3, NUI Galway. During that time, he was involved in the project of developing surrogate fuel mechanism (C3Mech), supported by Convergent Science Inc. and collaborated with the groups at NUI Galway, Lawrence Livermore National Laboratory, RWTH Aachen University and Politecnico di Milano. In September 2021, he joined HUST as a lecturer. He is currently focusing on ammonia combustion chemistry and ammonia combustion in engines.

Poster presentations

(Joint poster session and networking dinner of the satellite workshops - Saturday 21st July, 18.30-20.30)

FC1

Assessment and Validation of recent theoretical findings in Hydrogen combustion kinetics: Master Equation and Mixture Rules

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Keywords: Combustion, Hydrogen, Master Equation, Mixture Rules

The European Union has established a goal of reducing greenhouse gas emissions by at least 50% from 1990 levels by the year 2030. This reduction can be achieved by increasing the proportion of carbon-free fuels, such as hydrogen, in the energy mix.

Despite the significant progresses in kinetic models over decades, numerous adaptive parameters still exist, preventing a full reconciliation of microkinetic experiments and theory with macroscopic targets such as laminar flame speeds and ignition delay times. Recent theoretical advancements have permitted the precise description of numerous reaction rate constant parameters, including their pressure and temperature dependence, as well as the collisional parameters and the surrounding mixture effect.

In this study, a recently computed kinetic constant for the reaction $H + O_2 + M <=> HO_2 + M$ has been integrated within the CRECK model framework. Furthermore, a recently proposed non linear mixture formulation has been integrated into OpenSMOKE++ in order to independently handle the pressure dependency of each third body collider. This approach facilitates the formulation of the model in a more theoretically consistent manner. Moreover, the integration of this novel descripting formalism eliminates the dependence on a tunable parameter, thereby enhancing the model's reliability and predictive capability.Finally, the impact of the new non linear mixture rule formulation has been addressed with respect to the TROE formulation and the linear mixture rule formulation. Secondly, the newly computed value for the reaction rate constant has been adopted, and the kinetic model underwent an extensive automatic validation against a large data set of indirect experimental measurements publicly available within the SciExpeM framework.

The same workflow has been applied to other pressure dependent reactions. This, together with theory guided fitting of temperature dependent rate constants will produce a state of the art model reconciling theory, microscopic and macroscopic experimental targets [1].

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FC2

Hydrogen combustion: a new approach for the calculation of rate constants for termolecular reactions

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Keywords: Hydrogen combustion, termolecular reactions, collisional parameters, AI-TST-ME

A great accuracy in describing hydrogen reactivity is crucial considering the increasing interest in this molecule as an energy vector. It has though been shown there is significant uncertainty in the dependence on the bath gas of the rate constants of some key termolecular reactions. These reactions are typically expressed as a function of a reference reaction with a specific collider, and the rates with other colliders are obtained by means of corrective parameters (i.e. collisional efficiency) determined through the fitting of many sets of validation data. These parameters can vary substantially even between similar kinetic mechanisms, leading to non-unambiguous results. We propose here an approach to study hydrogen reactivity whose final aim is the full a priori revision of the elementary kinetics of hydrogen combustion by also implementing more rigorous mixture rules proposed in the literature.

First, high-pressure rate constants are determined using the ab initio transition state theory-based master equation approach (AI-TST-ME) as implemented in EstokTP. 1D master equation model was used with the collisional kernel described using the single exponential energy transfer model and recombination fluxes computed using Variable Reaction Coordinate Transition State Theory. The energy transfer parameters are then fitted for several colliders over a large set of experimental rate constant measurements, by interfacing the master equation simulator MESS to a non-linear regression software. Eight possible species (Ar, N_2, H_2, CO_2, H_2O, O_2, He, Kr) were investigated as bath gas, representing an exhaustive list of strong and weak colliders. Finally, rate constants for each individual collider were calculated and expressed in PLOG format for implementation in kinetic mechanisms. Collisional parameters determined in this work are in good agreement with the only other estimate of the collision parameters for the $H+O_2+M \rightarrow HO_2+M$ reaction found in the literature. The impact of the newly determined sets of rate constants of third body reactions in hydrogen combustion and of mixture rules from the literature are shown in the poster presentation FC1 by Dinelli et al.

FC3

Compact kinetic model for the combustion of NH_3/H_2 mixtures

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Keywords: NH_3/H_2 mixtures, parameter optimization, laminar burning velocities, jet-stirred reactor concentrations, burner stabilized stagnation flames

Ammonia's potential as a zero-carbon fuel and hydrogen carrier has ignited scientific interest in its application as a fuel in combustion systems. However, harnessing ammonia as a fuel source for energy applications presents notable challenges due to its low flammability and the potential for high emissions (Valera-Medina et al., 2018). Blending NH_3 with H_2 presents a prospect for enhancing combustibility, albeit with a notable increase in NOx emissions, particularly in fuel-rich conditions (Alnasif et al., 2023).

The development of burners, turbines, and engines is assisted by computational fluid dynamics (CFD) simulations, which require small-sized mechanisms. According to a recent review of the performance of ammonia combustion mechanisms (Szanthoffer et al., 2023), the San Diego 2018 mechanism (University of California), which has an exceptionally small size (21 species, 64 reactions), shows fair performance in predicting laminar burning velocities (LBV) and concentration data measured in jet-stirred reactors (JSR) under a wide range of conditions.

The current study focuses on developing a small and robust combustion kinetic mechanism for CFD simulations of NH_3/H_2 mixtures by optimizing the rate parameters of the San Diego 2018 mechanism using code Optima++ (Turányi et al., 2012; Papp et al., 2024; ReSpecTh.hu) with the FOCTOPUS optimization algorithm (Nagy, 2022). The San Diego 2018 mechanism was fitted to a large data collection of LBV and JSR concentration data (Szanthoffer et al., 2023; after pruning: 1259/1583 data points in 185/108 data series), as well as to a series of concentration measurements in burner-stabilized stagnation flame experiments with 70/30 vol% NH3/H2 mixtures (Hayakawa et al., 2021; 119 data points in 7 data series). In the error function, the total contributions of the three types of experiments were equally weighted to compensate for the imbalance in data collection. The refined model showed greatly improved prediction accuracy for the three types of experiments.

FC4

Identification of formaldoxime formed in CH_3+NO system: revealing key species in nitrogen- containing fuel combustion.

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Keywords: Formaldoxime; Chemical microreactor; Photoionization mass spectrometry; Elementary reaction; Methyl radical

Formaldoxime via reactions between methyl radical and nitric oxide was identified by exploiting a chemical microreactor with tunable vacuum ultraviolet (VUV) light in tandem with the detection of the ionized molecules by a high-resolution reflection time-of-flight mass spectrometer (Re-TOF-MS). Iodomethane, (CH_3I), and 2-chloropropane, ($(CH_3)_2CHCl$), were utilized as the precursors of methyl and isopropyl group to study the CH_3 + NO and $(CH_3)_2CH$ + NO radical – radical system. In this work, the photoionization efficiency (PIE) curve of the formaldoxime standard sample was measured to identify the presence of nitrosomethane (CH_3NO) and formaldoxime species. The formaldoxime formed via the reaction at the temperature of 923 K: $CH_3 + NO <=> CH_3NO <=> H_2C=NOH <=> HCN + H_2O$. Rearrangement via a 1,3-hydrogen shift or successive 1,2-hydrogen shifts requires high activation energy. Thus, formaldoxime is predicted to be relatively stable with respect to intramolecular rearrangement. This agrees with experimental results that formaldoxime is an observable dominant isomer. In $(CH_3)_2CH$+ NO system, acetone oxime was produced via $(CH_3)_2CH + NO <=> (CH_3)_2C=NOH$ through the transition state of a four-membered ring is not dominant, compared to the hydrogen extraction reaction of NO to generate HNO and C_3H_6. The generation of fulminic acid (HCNO) was found in both pyrolysis systems, verifying that the reaction path, $3CH_2 + NO <=> HCNO + H$, is dominant in product formation.

FC5

Plasma-Flow Coupling in Nanosecond Repetitively Pulsed Discharges: Mechanism and Morphology in an Air Crossflow.

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Keywords: plasma assisted combustion, chemistry-flow coupling, local thermal equilibrium, plasma chemistry

Nanosecond repetitively pulsed discharges (NRPDs) using a pin-to-pin electrode configuration are extensively investigated as a method of stabilizing combustion, especially in severe conditions. NRPDs can be particularly effective for enabling the use of renewable fuels such as hydrogen and ammonia, which add new challenges and whose combustion technologies are rapidly developing.

Different regimes of NRPDs have been highlighted in previous works, and are affected by pulse repetition frequency, applied voltage, and interaction with flow velocity, composition, and temperature. These interactions between plasma parameters and flow can have significant variance in outcomes, and the transitions from regime to regime need to be better understood. Shcherbanev et al. [1] found that in hot conditions, the discharge curves in the flow direction. This happens due to plasma-flow coupling: the gas is heated by the plasma, the heated region is then convected downstream. The subsequent breakdown happens in the region of reduced gas densities, thus curving the discharge under these conditions. Vibrational-translational (VT) energy transfer is key to this effect, which significantly affects the efficiency of ignition.

A similar effect was observed in cold conditions, where local thermal equilibrium (LTE) can be produced on a nanosecond timescale [2]. The mechanism will differ from hot conditions due to different energy branching. In LTE plasmas, vibrational levels might not play key roles because of the high degree of molecule dissociation, leaving mostly atoms and atomic ions. This work uses schlieren imaging, discharge visualization, and energy measurements to investigate this coupling under atmospheric air conditions when LTE plasma occurs. The findings can be important for both high-pressure, high-temperature conditions typical of engines, and for chemistry applications at low temperatures and pressures.

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FC6

Flame Chemistry: Do we understand how double-base propellants burn?

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Keywords: Double-base propellants, reaction kinetics mechanism, ignition delay time, laminar flame speed, burning rate model

Double-base propellants are a class of solid propellants that are widely used in modern rocket technology, in which the propellants' combustion performance has a significant impact on the launch and range of rockets. Aiming to deeply understand the combustion performance of double-base propellants, the thermochemical properties of important species and kinetic parameters of key reactions in the pyrolysis and combustion processes of double-base propellants are obtained in this study through high-level quantum chemical calculations. The M06-2X/6-311++G(d,p) level of density function theory was used for the geometry optimization, vibrational frequency, and dihedral scan calculations. Single point energy calculations were carried out at the CCSD/cc-pVXZ (where X=T, Q) level of coupled cluster theory. Based on the computational results, a detailed reaction kinetic mechanism for double-base propellant is constructed. The measurements of ignition delay time and laminar flame speed were also performed to optimize the constructed reaction kinetic mechanism. The key elementary reactions and reaction pathways controlling the pyrolysis and combustion of double-base propellant were analyzed and regulated. Finally, by coupling the combustion kinetic model with the gas-condensed two-phase, a prediction model of double-base propellant combustion performance is developed, which is capable of realizing the accurate prediction of the combustion performance of dual-base propellant under a wide pressure range of 0.1 MPa ~ 30 MPa.

FC7

Development of a fast screening method for soot tendency evaluation.

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Keywords: Soot, Yield Soot Index (YSI), MBMS, Flow Reactor, SAF

Sustainable aviation fuels (SAFs) mitigate emissions associated with CO_2, and non-CO_2 effects [1]. A comprehensive understanding of pollutant formation during the combustion of SAFs, especially soot formation, is crucial for further fuel development and optimization. Fast and efficient methods for measuring parameters like the soot formation tendency of fuels are essential to achieve this aim.

A novel screening method is currently under development to provide a fast overview of the soot tendencies of different fuels or fuel components. Its aim is to enhance the efficiency of measuring the soot tendency correlated to the yield sooting index (YSI) [2], through reduced sample volumes, automatization, and increased throughput in shorter time compared to existing experiments. The method involves the measurement of soot precursor species in the DLR's flow reactor coupled with molecular-beam mass spectrometry (MBMS) and a time-of-flight mass spectrometer for the analytical data acquisition [3]. The enhancements are further achieved by integrating a standalone autosampler system into the experimatal setup, and adopting a new method for evaluating the measurement data.

Based on previous studies regarding the correlation between hydrogen content, soot precursors, and soot emissions of a fuel [4], the proposed approach establishes a reliable link between soot precursors and the YSI. A first experimental series was performed for multiple samples representing different hydrocarbon classes from n-alkanes to di-aromatics as pure fuel components. The signal intensities for different soot precursor species ($>C_6H_6$) can be correlated with the YSIs from the existing database. With establishing a relation based on the experimental data, correlation of further measurements with a respective YSI value can be concluded.

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FC8

Predicting real-fuel combustion and particulate emissions using a functional-group-based approach (FGMech)

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Keywords: FGMech, PAH formation, Real fuel combustion

Accurate predictions of gas-phase and particulate emissions from the combustion of real fuels are challenging. The present study aims to develop a procedure based on a functional-group approach (FGMech) for generating compact kinetic mechanisms of real fuels, capable of predicting polycyclic aromatic hydrocarbon (PAH) and soot emission. This model comprises four sub-mechanisms: 1) a functional-group-based lump mechanism named FGMech [1]; 2) a base mechanism for the chemistry of fundamental fuels, i.e., AramcoMech 3.0 [2]; 3) a PAH mechanism [3] with additional important pathways; and 4) a surface kinetic mechanism describing the soot inception, absorption, surface growth, and oxidation. In addition, PAH formation pathways with high uncertainty of rate constants are optimized by Optima++ [4]. This model is then extensively validated against experimental measurements of ignition delay time (IDT), laminar burning velocity (LBV), species mole fraction, laser-induced fluorescence (LIF), laser-induced incandescence (LII), and soot volume fraction (SVF) in laminar premixed and counterflow diffusion flames for fuels ranging from ethylene to primary reference fuels and real fuels in the gasoline-diesel range. The results show that adding PAH and soot surface sub-mechanisms does not noticeably change the IDT and LBV for various fuels, meaning that the validation of FGMech + AramcoMech 3.0 still holds for our current model. The predictions by the current PAH sub-mechanism are generally in good agreement with experimental mole fractions for species up to pyrene in flames of simple fuel (e.g., ethylene) and LIF measurements for the combustion of fuel surrogates. The surface kinetic model could also provide reasonable trends for measured SVF and LII. Furthermore, the gas-phase mechanism is reduced by adopting a combination of automatic mechanism reduction and species lumping, which provides a solid foundation for future computational fluid dynamics (CFD) study of complex fuel mixtures.

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FC9

Advancing ammonia-hydrogen combustion reaction kinetics: Informative experimental datasets constructed through global-sensitivity-based clustering

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Keywords: Ammonia, Clustering, Global sensitivity, Experimental design

In recent years, the combination of ammonia and hydrogen has emerged as a promising, zero-carbon energy source. Existing experimental data on their combustion are abundant, but challenges exist due to redundancy and gaps in critical reaction kinetics information. This study utilizes a global-sensitivity-based clustering algorithm to create informative experimental datasets with cluster exemplars. The goal is to refine existing data and guide future experimental efforts in the field of ammonia/hydrogen combustion.

The study follows a three-step approach. Firstly, global sensitivity analysis using an ANN-based HDMR algorithm identifies sensitivity indices for each experimental condition. Secondly, the affinity propagation clustering algorithm groups conditions into clusters and selects exemplars. Finally, the exemplar dataset is used to optimize a model, demonstrating the effectiveness of dataset construction. This method is applied to two parameter spaces with 2491 and 5950 data points. The main distinction between the two spaces lies in whether the experiments have been conducted up to the present time.

In total, 2491 data points are classified into 29 clusters, with an informative dataset of 29 exemplars used for model optimization, significantly enhancing predictive performance. Analysis reveals focus on 22 parameters out of 275. To uncover overlooked reaction kinetics, the dataset is expanded to 5950 conditions, with thirteen previously insensitive parameters now showing sensitivity. Optimizing with this expanded dataset enhances performance and uncovers insights.

The study presents informative experimental datasets utilizing the affinity propagation clustering method with global sensitivity coefficients. These datasets address information overlap and offer insights for acquiring additional information through future experiments. The methodology can be applied to other fuel systems to advance chemical kinetics.

FC10

Megahertz visualization of a non-marginal hydrogen-air detonation using multi-pulse Rayleigh scattering

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Keywords: laser diagnostics, high-speed visualization, CJ detonation

The detonation structure is multidimensional (3D) and cannot be easily characterized by line-of-sight integrated techniques, outside of narrow channel experiments. In most studies dealing with narrow channels, the detonation is considered as marginal because its structure and its propagation speed are altered by wall confinement effects. Despite this limitation, high-speed (>1 MHz) schlieren measurements in narrow channels have provided significant information about the detonation dynamics. Some laser-based diagnostics, such as planar laser-induced fluorescence (PLIF) or Rayleigh scattering, are not line-of-sight integrated and can provide information about the cross-section of a non-marginal detonation (i.e., detonation propagating at CJ speed with multiple cell in the thickness of the channel). This study aims to assess the possibility of using a Nd:YAG laser cluster (four individual Nd:YAG lasers) to conduct high-speed visualization (2.5 MHZ) of non-marginal H_2-air detonations, at 25 kPa and 293 K, with multi-pulse Rayleigh scattering. From the four Rayleigh pulses, the local speed is directly measured by the front displacement between each pulse ($\approx$ 400 ns), while the average speed evolution along the cell cycle is reconstructed from multiple visualizations. Qualitatively, results are in agreement with previous measurements obtained in narrow channels. Quantitatively, the speed decay is more pronounced in narrow channel experiments than in the current measurements, which tends to confirm the effect of the wall confinement on the speed dynamics within the cell cycle. This diagnostic is complementary to the existing visualization techniques because it is not restricted to narrow channel experiments, it can be applied to a large range of detonation conditions, and it has no theoretical limits on the visualization frequencies.

FC11

Insights into the effect of CO vibrational relaxation on the non-equilibrium combustion measurements with a state-to-state kinetic model

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Keywords: vibrational relaxation; non-equilibrium reaction kinetics; shock tube measurements; mechanism optimization

Conventional combustion reaction kinetics models are constructed using the assumption that the distribution of particles across energy levels conforms to the equilibrium Boltzmann distribution. However, extreme conditions, such as rapid reactions or hypersonic velocities, can induce non-equilibrium excited internal energy modes of the molecules, challenging the accuracy of existing models in predicting combustion characteristics. Drawing inspiration from the seminal work of Wooldridge et al. [1], this study advances a comprehensive state-to-state kinetic sub-model for CO vibration relaxation involving ground and vibrationally excited states. Recognizing and using the non-equilibrium experimental data from a large amount of shock tube measurements [2], the Arrhenius parameters are constrained, and the kinetic sub-model is optimized. Integrating this CO state-to-state kinetics sub-model with classical reaction mechanisms (e.g., Aramco-2.0) improves the accuracy of predicting non-equilibrium combustion kinetic measurements, while the mechanism performance of the reproduction on equilibrium measurements is not significantly affected. The present study suggests that incorporating a state-to-state model could offer a novel approach to understanding combustion kinetic behavior and enhancing model performance. This approach improves the reproduction of some of the measurements without compromising its ability to reproduce other measurements, where the assumption of the Boltzmann distribution is valid.

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FC12

Characterizing the interaction of N_2O and CO with and without hydrogen addition using outwardly propagating spherical flames

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Keywords: Carbon monoxide; Nitrous oxide; NOX reduction; Flame instability; Laminar burning velocity; Kinetic model

Nitrous oxide (N_2O) is the third most important long-lived greenhouse gas and plays a role as the principal source of stratospheric nitric oxide, as well as the major scavenger of ozone. Nowadays, the utilization of NH_3 as a fuel underscores the need to reduce N_2O emission under flame conditions. Therefore, there is a need to understand the interaction between N_2O and low-carbon fuels, especially carbon monoxide and hydrogen. This study pioneers the utilization of outwardly propagating spherical flame method to investigate the laminar flame propagation of CO/N_2O mixtures at the initial pressure (P_u) of 2 atm, initial temperature (T_u) of 298 K and equivalence ratios ranging from 0.6 to 1.8. Additionally, the study delves into the interaction of N_2O and CO in the presence of H_2, examining the $CO/H_2/N_2O/N_2$ flame under similar conditions. Unlike CO/O_2 system, successful hydrogenic-free CO spherical flame propagation with N_2O as oxidizer was demonstrated. Observations revealed an unsteady transition from weak flame to normal flame in both CO/N_2O and $CO/H_2/N_2O$ fuel-rich flames, while the pulsating instability of $CO/H_2/N_2O$ flames occurring in moderate lean conditions. The accelerated laminar burning velocities (LBVs), increased flame thickness, and larger Markstein lengths in $CO/H_2/N_2O/N_2$ flames suggest a significant enhancement in thermal diffusivity due to hydrogen addition. Notably, the LBVs of "dry" CO/N_2O and $CO/N_2O/N_2$ flames within the closed combustion vessel of this study were found to be substantially lower than previously reported results using an open Bunsen-type flame, i.e., the literature reported LBVs of 50% CO/50% N_2O flames is 3.3-4.5 times higher than the currently measured value. The measured LBVs underscore the necessity for further examination of the rate of the controversial radical exchange reaction $CO+N_2O=CO_2+N_2$ (R1). Comparison of the measured data with the predictions of literature kinetic models reveals the inadequacy of existing models. The proposed model, featuring an updated $CO/H_2/N_2O$ subset, enhances predictability and highlights the intricate chemistry.

FC13

Understanding the Effect of Stimulated Raman Scattering on NH-PLIF Measurements in Ammonia Spray Flames

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Keywords: Liquid ammonia, ammonia spray flame, stimulated Raman scattering, NH-PLIF.

As ammonia gains importance as a green fuel, particularly in its liquid state, due to its carbon-free nature, high energy density, and cost-effectiveness, there is an increasing need to thoroughly understand the combustion dynamics of liquid ammonia using advanced optical and laser diagnostics. For example, planar laser-induced fluorescence (PLIF) of the NH radical has been employed to effectively characterize the fuel consumption layer within the reaction zones of ammonia combustion. However, these studies focus on flames where ammonia is injected in the gas phase, while injecting it in the liquid phase offers practical advantages. It is crucial to verify the feasibility of NH-PLIF in ammonia spray flames, as other techniques have proven difficult to apply due to the presence of droplets. Therefore, this study focuses on experimentally investigate the stimulated Raman-type interferences that may occur during the NH-PLIF measurements in ammonia spray flames. These interferences, caused by the resonance of a spontaneous Raman scattering signal in the liquid fuel droplets when illuminated by the laser, which can degrade the quality of the desired NH fluorescence images. Therefore, it is crucial to (i) quantify experimentally the impact of these interferences in ammonia spray flames (ii) propose possible solutions to mitigate these interferences. These two objectives form the core of this study. The experiments were conducted in a confined burner operating at ambient pressure and room temperature. In this setup, liquid ammonia was atomized using a pressure swirl atomizer and co-fired with a lean swirl premixed methane flame. The flame characterization was performed using a Nd:YAG laser, two ICCD cameras, and a Princeton Instruments spectrometer.

FC14

Investigation of the thermal decomposition of C_4 – C_6 alkenes

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Keywords: UV absorption diagnostic, alkene, thermal decomposition, rate rules, model improvement

Alkenes are crucial intermediates in hydrocarbon pyrolysis, oxidation, and polycyclic aromatic hydrocarbons (PAHs) formation. This study investigates the thermal decomposition of C_4-C_6 monoenes and dienes using sensitive UV diagnostic techniques within the wavelength range of 212.5-220 nm.

Initially, the site-specific thermal decomposition of C_4-C_6 monoenes (1-butene, 1-pentene, 1-hexene, and 4-methyl-1-pentene) was investigated. The reactions were monitored by tracing the time-histories of the product allyl radical using a sensitive UV diagnostic at around 220 nm. The rate coefficients were extracted by simulating the measured absorbance profile with a detailed mechanism, and reported in Arrhenius expressions. Measurements of these four molecules facilitated the development of rate rules covering the decomposition of allylic-primary, allylic-secondary (S21 and S22), and allylic-tertiary C-C bonds. These rate rules benefit accurate modeling of 1-alkenes, branched alkanes, and biofuels containing double bonds.

Next, the thermal decomposition reactions of C_4-C_6 dienes (1,3-butadiene, isoprenene, and 2,3-dimethyl-1,3-butadiene) were examined. Absorption cross-sections of the dienes at selected wavelengths (1,3-butadiene at 212.5 nm, isoprene at 215.8 nm, and 2,3-dimethyl-1,3-butadiene at 220.5 nm) were measured. Subsequently, the decomposition of the dienes was investigated by monitoring the decay of the reactants. Overall rate coefficients were determined from the initial slope of the reactant decay and presented through Arrhenius expressions. Decomposition of the molecules was observed at temperatures above approximately 1350 K, and all three molecules exhibited similar activation energy. At around 1800 K, 2,3-dimethyl-1,3-butadiene decomposed twice as fast as isoprene and four times faster than 1,3-butadiene.

Furthermore, the measured rate coefficients and rate rules were incorporated into various existing models. Our data significantly enhanced the fidelity of alkene and biofuel kinetic models. The UV absorption diagnostic proved to be a powerful tool for conducting quantitative, time-resolved, highly sensitive, and non-intrusive kinetic experiments.

FC15

Forward and reverse uncertainty analyses for RRKM/master equation based kinetic predictions: A case study of ethyl with oxygen

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Keywords: RRKM/ME model rate coefficients; branching ratio; forward uncertainty analysis, reverse uncertainty analysis

In the realm of combustion kinetic modeling, the norm involves employing thousands of reactions to delineate the chemical conversion of hundreds of species. Notably, theoretically predicted rate coefficients and branching ratios, derived through the RRKM/master equation (ME) model, play an increasing role in kinetic modeling. Thus minimize the uncertainty of theoretical prediction across wide working conditions is crucial to refine a kinetic model. The present study takes C_2H_5 + O_2 reaction system to show that combined forward and reverse uncertainty analysis can be used to further constrain calculated rate coefficients and branching ratios, which were already calculated by high-level quantum chemistry methods. Forward global uncertainty analysis with the artificial neural network-high dimensional model representation (ANN-HDMR) method is employed to select key parameters affecting total rate coefficients of C_2H_5 + O_2 and branching ratios of C_2H_5 + O_2 = C_2H_4 + HO_2 (C1). Reverse uncertainty analysis with Bayesian method was then applied to refine the key input parameters based on experimental data at working conditions selected by sensitivity entropy. The above analysis process was carried out based on the integrated framework for experimental design and combustion kinetic model optimization: OptEx. Although the target RRKM/ME model system was built on high level theoretical calculations, the combined forward and reverse uncertainty analyses are still able to reduce uncertainty of predicted branching ratios for C_2H_5 + O_2 = C_2H_4 + HO_2 across a wide range of working conditions. Specifically, the uncertainty of branching ratio has been reduced from 1.52 to 1.36 at 298 K and 1 Torr. The analysis process proposed in the present work effectively extrapolates the constrain ability of accurate measured data at one condition to wide working conditions based on the RRKM/ME model.

FC16

Investigation into Hydrogen Integration within High-Temperature Oxyfuel Processes

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Keywords: natural gas-hydrogen mixtures; oxyfuel flame; optical and temperature investigation, exhaust gas

Transitioning from natural gas to hydrogen as a fuel is crucial in high-temperature applications. This study investigates the impact of hydrogen on natural gas flames in oxyfuel combustion.

A premixed oxy-fuel flame of hydrogen-methane blends was stabilized under atmospheric conditions. Two scenarios were examined: low hydrogen levels (0-35 vol.%) and high hydrogen levels (50-100 vol.%). Using a premixed burner at three power levels, flame characteristics were analyzed through optical, spectroscopic, and thermal measurements. Hydrogen-methane-oxygen mixtures at different equivalence ratios ($\phi = 0.8 - 1.2$) were tested to observe changes in flame morphology, temperature distributions, and species formation.

A larger non-premixed natural gas-oxygen flame with varying hydrogen admixture (0-100 vol.%) was also investigated. The burner's power ranged from 10 kW to 50 kW, tested as both a free-flame and within a multi-segment combustion chamber. A camera system captured visible and ultraviolet signals from the combustion zone, while type S thermocouples recorded temperature profiles. Exhaust gas components (CO_2, NOx, O_2) were measured across different fuel compositions and equivalence ratios.

The study assessed hydrogen's impact on methane oxy-fuel combustion using a single-flame burner. Results showed higher temperatures with increased hydrogen content, shortened flame lengths, and changes in emitted spectra. Up to 35 vol.% hydrogen had minor effects, but 100 vol.% caused significant shifts, challenging flame stabilization and requiring adjustments.

For the larger-scale flame, the burner transitioned from natural gas to hydrogen without structural changes. Flame lengths slightly reduced, and the flame root widened. Elevated OH* radical concentrations and increased flame temperatures were noted, benefiting production processes but complicating glass chemistry. Pure hydrogen-oxygen combustion exhaust mainly comprised oxygen, with rising NOx levels as hydrogen content increased. Adding nitrogen to the oxidizer further increased NOx values, emphasizing the need for process-oriented evaluations.

FC17

Burning hydrogen with sand dilution: Combustion mechanisms in packed bed arrangements

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Keywords: natural gas-hydrogen mixtures; oxyfuel flame; optical and temperature investigation, exhaust gas

Hydrogen (H_2) combustion in fluidised beds of quartz sand (SiO_2) is a promising solution to decarbonise industrial heating. However, reactions between H_2 and SiO_2 are not well known. To study the effects of SiO_2 surfaces on H_2 combustion, H_2-air combustion was investigated in an empty reactor tube and a packed bed of SiO_2 particles (355-425 µm) for a range of reactor temperatures. In the empty reactor tube, water vapour (H_2O) yield increased sharply at 600°C. In the packed bed, combustion onset was observed at 350°C, and H_2O yield increased gradually with temperature. Enhanced low-temperature combustion suggested a heterogeneous mechanism involving solid surfaces. The effect of available surface area was studied in packed beds of smaller (125-225 µm) and larger (1400-1700 µm) SiO_2 particles. H_2 conversion diminished by increasing the total surface area of SiO_2, demonstrating that combustion does not occur entirely on surfaces. The void fraction of packed beds revealed that the highest H_2 conversion was associated with the shortest residence times in the bed of large particles. As the size of interstitial voids in packed spheres scales linearly with sphere diameter, combustion may have been promoted within voids of beds of large particles.

As chain initiation (H_2+O_2->H+HO_2) has a high activation energy, low-temperature combustion might be enabled by the catalytic dissociation of H_2 or O_2 on silica, resembling a heterogeneous pathway for chain initiation. Above 200-400°C, dominant chain branching reactions, O+H_2>OH+H and H+O_2>OH+O, have characteristic times shorter than the residence time in voids. Between 400 and 800°C, these characteristic times are comparable to diffusion times of H and O radicals from voids to walls, suggesting active competition between branching reactions within voids and chain termination on surfaces. These findings demonstrate that H_2 may readily burn in the particulate phase of a fluidised bed, especially in beds of large particles.

FC18

Cyclooctane – A potential high-performance molecule for optimizing fuels and emissions

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Keywords: Cyclooctane, reaction mechanism, flow reactor

Reducing pollutant emissions is a key aspect of fuel design and optimization. There are many ways to reduce emissions, from fuel production, to sustainable resources and technologies, to engine design modifications to the targeted fuel design. In this context, we aim to investigate various high-performance molecules - promising new fuel components that have the potential to reduce emissions due to their molecular structure and composition. Here, the reaction kinetics of cyclo-octane is investigated experimentally using the DLR high temperature flow reactor [1] and numerically using the DLR Concise reaction mechanism for fuels [2]. In comparison to well investigated cyclo-hexane and its alkyl derivatives, surprisingly studies on combustion chemistry of larger ring cyclo-alkanes has remained untouched. In a general conversion route, cyclo-hexane undergoes dehydrogenation in six reaction steps creating benzene. An analogous dehydrogenation route of cyclo-octane creates cyclo-octatetraene. Unlike benzene, cyclo-octatetraene is not aromatic and its reactivity is rather characteristic to polyene. The impact of this small change in the molecular structure on further PAH growth and subsequent to soot emissions is revealing new scientific insights.

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FC19

Investigation of the oxidation of dimethyl ether/air and dimethyl ether/hydrogen mixtures by chemical kinetics modeling

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Keywords: dimethyl ether, dimethyl ether / hydrogen mixtures, quantitative mechanism comparison, experimental data collection, detailed combustion mechanism

Dimethyl ether (DME, CH_3OCH_3), the smallest compound in the oxymethylene ether group, is an attractive alternative to conventional diesel fuel for compression-ignition engines. The aim of this work is the quantitative comparison of recent detailed DME oxidation mechanisms on a comprehensive experimental data set.

Detailed DME oxidation mechanisms were collected from the literature. The experimental data collected were encoded in ReSpecTh Kinetic Data format [1] XML files. The chemical kinetic simulations were performed with program Optima++ and solver package Cantera.

The performances of 21 existing reaction mechanisms are compared quantitatively on a wide range of DME and DME/H_2 oxidation experiments including concentration measurements in jet-stirred reactor (JSR), flow reactor (FR) and burner-stabilized flames (BSF); ignition delay measurements in shock tubes (ST) and rapid compression machines (RCM), and laminar burning velocity measurements. The experiments covering wide ranges of equivalence ratio, pressure and temperature were collected from 75 publications. Ignition delay time and laminar burning velocity measurements could be reproduced well by the models, while worse results were obtained for the concentration measurements. Performances of the models on reproducing experimental data were analysed according to experiment types and condition ranges using quantitative measures.

The overall best performing mechanism was NUIGMech1.1-2020 [2], although it also could not well reproduce the JSR and BSF data. The simulation results for some JSR and FR measurements were sensitive to the initial temperature used in the calculations, so the effect of experimental temperature uncertainty on mechanism performance should also be analysed in detail.

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FC20

Recent advancements in the reaction kinetics branch of the ReSpecTh Information System

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Keywords: searchable database, laminar burning velocity measurements, concentration measurements burner stabilized flames, detailed reaction mechanisms, computer programs

The continuous development of the REaction kinetics branch of the ReSpecTh Information System [1] aims ReSpecTh to be the biggest collection of searchable direct and indirect combustion experimental data, detailed combustion mechanisms, and related computer programs.

Experimental data are encoded in ReSpecTh Kinetics Data format [2] XML files and stored in a searchable database. Thematic collections of detailed reaction mechanisms provide a unique opportunity to use recent mechanisms for various fuels in CHEMKIN, Cantera, and OpenSMOKE++ native formats. Computer programs (like Optima++, FluxViewer++, Minimal Spline Fit, SEM (Simulation Error Minimization reduction code), ReactionKinetics) serve the various needs of the researchers related to chemical kinetics problems. The new front-end of ReSpecTh.hu provides the users with a more efficient information collection through a modern interface.

The amount of experimental data stored in the ReSpecTh database increases continuously. Beside the homogeneous measurements (148147 data points in 3778 experimental series)), the database contains large amount laminar burning velocity measurements (13105 data points in 1462 experimental series) and concentration measurements in burner stabilized flames (1928 data points in 110 experimental series). The data collection includes data for the combustion of hydrogen, carbon monoxide, methane, ethylene, ammonia, methanol, ethanol and butanol, and measurements on the $H_2/O_2/NOx$ and methanol/NOx systems. The number of downloadable detailed mechanisms is 193. The ReSpecTh information system is becoming more and more popular, and currently, it has 879 users.

All information, data, and computer codes are freely available to researchers and developers. Our research group aims to continue developing and extending this information system in cooperation and collaboration with other researchers to benefit the whole research community.

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FC21

Balancing Accuracy and Computational Cost for Quantum Mechanical Thermochemistry

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Keywords: thermochemistry, benchmarking, quantum chemistry, enthalpy of formation

Accurate thermochemical properties, such as standard enthalpies of formation, are crucial for kinetics models to predict the behavior of chemical systems reliably. In our previous work [1], we implemented and compared two popular bond additivity correction (BAC) schemes, Petersson-type and Melius-type BACs, along with isodesmic reaction (IDR) methods, in the open-source Arkane software. This work significantly expands the scope of our investigation by fitting Petersson-type and Melius-type BACs for over 200 model chemistries, spanning various electronic structure methods, including semiempirical methods, density functional theory (DFT), and wave function theory (WFT). By extensively benchmarking these correction schemes, we aim to identify the most accurate and computationally affordable combination of methods for obtaining reliable thermochemical properties.

Our results reveal that the accuracy achieved by applying Melius-type and Petersson-type BACs is largely indistinguishable, but the level of improvement depends heavily on the chosen level of theory and certain molecular features, primarily total charge. The most cost-effective strategy is to use a minimal level of theory for geometry optimization and calculate the single point energy with DLPNO-CCSD(T)-F12, followed by applying a BAC. This strategy achieves a mean absolute error (MAE) of < 2 kcal/mol with a semi-empirical geometry (e.g., AM1) and < 1 kcal/mol with a relatively inexpensive DFT geometry (e.g., B97-1/6-31G(D)). Both types of BACs offer the most significant accuracy improvement for zwitterionic species. Anionic species benefit strongly from diffuse basis functions like those in def2-SVPD before and after applying a BAC. These findings provide valuable insights into selecting the most suitable combination of methods for obtaining accurate thermochemical properties while minimizing computational costs.

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FC22

Model reduction assisted parameter optimization of the ethylene chemistry in the AramcoMech 2.0 combustion mechanism

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Keywords: Ethylene combustion, Ignition delay time, Laminar burning velocity, Mechanism reduction, Mechanism optimization

In this work, a kinetic parameters optimization of the ethylene chemistry in the AramcoMech 2.0 mechanism (493 species and 2716 reactions) was carried out against a large collection of indirect experimental data. The data collection consisted of ignition delay time measurements in shock tubes covering a temperature range of 930-2230 K and a pressure range of 0.28-63.3 atm, laminar burning velocity measurements at preheat temperatures from 298 to 650 K, and pressures from 0.5 to 10 atm. Due to the large size of the model and the data collection, direct optimization was not feasible, therefore we applied the Model Reduction Assisted Parameter Optimization procedure. First, using the Simulation Error Minimization Connectivity Method, a reduced mechanism with 75 species and 612 reactions was developed that performs similarly to the detailed mechanism regarding the indirect measurements. This smaller model could be simulated much faster enabling efficient optimization with moderate computational effort on the large number of experimental targets. Then, influential reactions of the reduced model were identified using the novel active parameter selection method, which is based on principle component analysis of the local sensitivity matrix scaled with experimental data uncertainty and parameter uncertainty. A total of 79 Arrhenius parameters (ln(A), n, E/R) in 16 reactions were identified and optimized within their prior uncertainty domain against the indirect experimental data collection. Finally, the optimized parameters were transferred to the original AramcoMech 2.0 mechanism, whose performance was shown to improve in a similar fashion as that of the reduced model. The posterior uncertainty limits of the optimized rate coefficients were calculated based on direct and indirect measurements. These were typically much narrower compared to the prior ones.

FC23

Experimental and numerical study of ammonia/methane blends combustion and oxidation

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Keywords: Ammonia, *methane, molecular-beam mass-spectrometry, jet-stirred reactor, detailed combustion mechanism*

Recently, ammonia received attention as a prospective carbon-free fuel. However, in spite of the well-established infrastructure of its storage, transportation and utilization, pure ammonia is not suitable to be used as an individual fuel. To improve ammonia combustion properties methane can be used. Therefore, the extension of experimental database on ammonia/methane combustion and oxidation is of crucial importance.

In the present work the structure of ammonia/methane flames (ϕ=0.8, 1.0, 1.2) was measured at 1, 3 and 5 atm. Flames were stabilized on a flat burner (T=368K). The ammonia/methane ratio was 1/1. The measurements of flame structure were performed using molecular beam mass-spectrometric setup with soft electron impact ionization. Temperature profiles were measured with thin S-type thermocouples. The oxidation of ammonia/methane blends (ϕ=0.5, 1.0, 2.0) was studied using jet-stirred reactor, residence time was 1s throughout the experiments and temperature value was set from 800 to 1300K. Similar to the experiments on flame structure the ammonia/methane ratio was 1/1. Numerical modeling was performed with the CHEMKIN package. Several recently published chemical-kinetic models were tested.

Comparison of experimental and numerical data for concentrations of the different species, forming during the combustion and oxidation of ammonia/methane blends, was made. The flame structure data is found to be in a satisfactory (within the experimental uncertainty) agreement in general. In this part of the work, an analysis of the effect of pressure and equivalence ratio on the concentrations of intermediates was done. Experiments in a jet-stirred reactor, on the contrary, have shown that the tested models predict different temperature range for ammonia and methane oxidation. Based on the jet-stirred reactor data, the influence of equivalence ratio on the species formation and on the onset and offset temperature values of ammonia and methane oxidation were examined.

FC24

Predictive Mechanistic Modeling of PFCA Flame Kinetics and Thermochemistry

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Keywords: PFAS, PFOA, flame, kinetics, mechanism

Flame chemistry for C_1-C_9 fluorocarboxylic acids (PFCAs) has significant differences relative to hydrocarbon combustion. Predictions for PFCAs mixed into methane flames are particularly relevant to the combustion and incineration of per- and polyfluoroalkyl substances (PFAS). Low-hydrogen fluorocarbons interfere with hydrocarbon flames and suppress them while generating HF and products of incomplete combustion that can be toxic and corrosive. Kinetics and products thus are both of interest. The strong C-F bonds and the lone H in PFAS acids diminish the roles of abstraction that are so important for alkane combustion chemistry. The latter is dominated by H, O, OH abstraction of H and β-scission of the resulting alkyl radicals, where abstracting radicals come from the β-scissions and chain-branching through $H+O_2=O+OH$ and $H_2+OH=H+H_2O$. A striking contrast is the importance of thermal pericyclic and homolytic decompositions, which substantially lead to perfluoroalkyl radical β-scissions. In PFCA/methane flames, these radicals can abstract H from the CH_4 or from combustion-produced H_2O, opening diverse additional channels.

FC25

Advancing Reaction Kinetics and Thermochemistry Prediction through High-Throughput Quantum Chemistry and Graph Neural Networks

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Keywords: Foundational quantum chemical dataset, Automated transition state generation, Graph neural network for thermokinetic property prediction

We present our work in generating a comprehensive quantum mechanical (QM) dataset for advancing the understanding of reaction kinetics and thermochemistry relevant to combustion chemistry and alternative fuel applications. Our open-source high-throughput computational chemistry workflow has produced an extensive dataset comprising over 340,000 open- and closed-shell reacting species, 200,000 transition state (TS) geometries and frequencies optimized at both the GFN2-XTB semi-empirical and ωB97X-D/def2-SVP density functional theory (DFT) levels of theory, along with DLPNO-CCSD(T)-F12d/def2-TZVP reaction barrier heights, bond-additivity corrected enthalpies, and more than 100 million COSMO-RS solvation free energies in over 300 common solvents. The unparalleled scale and depth of this dataset can potentially lead to unprecedented insights into advancing combustion and fuel research.

Moreover, our poster highlights the automated TS generation capabilities enabled by our workflow. We demonstrate how this automation accelerates the exploration of complex reaction networks and enables unprecedented insights into temperature- and solvation- dependent reaction kinetics. Furthermore, by leveraging this extensive dataset and state-of-the-art Chemprop Directed Message Passing Neural Network (D-MPNN) models, we present promising preliminary results in accurately predicting thermochemistry and reaction barrier heights. The combination of high-throughput quantum chemistry and advanced graph neural networks demonstrates immense potential for accelerating the development of accurate and detailed chemical kinetic mechanisms. These advancements are crucial for designing efficient combustion devices and assessing the performance of novel sustainable fuels. We anticipate that our open-source dataset and software will not only contribute to advancing the fundamental understanding of reaction kinetics and thermochemistry, but also further stimulate and enhance collaboration within the combustion chemistry community.

FC26

Identification of well-parameterized reaction steps in detailed combustion mechanisms – a case study of ammonia/air flames

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Keywords: ammonia combustion, laminar burning velocity, detailed reaction mechanisms, well-parameterized reactions, mosaic mechanisms

The typical experience with testing detailed reaction mechanisms is that some mechanisms describe the indirect experimental data well under most conditions but are ill-performing under other conditions. Some other mechanisms are not very good under most conditions but reproduce the data well under other conditions. A possible reason is that if a mechanism is accurate under some conditions, then all highly important reaction steps at these conditions are present with good rate parameters, or at least the critical ratios of certain rate coefficients are correct. If we have a large collection of experimental data and many tested reaction mechanisms, we may identify which are the well-parameterized reaction steps in each mechanism. A better, unified mechanism ("mosaic mechanism") may be obtained by identifying the overall best-performing mechanism and loaning the most important reaction steps or their rate parameters from another mechanism having good performance under the conditions where the overall best model is ill-performing. In this case, the selected reactions presumably have good rate parameters in the other mechanism. This procedure does not require the fitting of rate parameters (i.e. mechanism optimization). In this work, a new algorithm is developed based on this presumption and the quantitative evaluation of the performances of mechanisms as a function of the n relevant experimental conditions. The algorithm is successfully applied to eight recent detailed combustion mechanisms and a comprehensive collection of NH_3/air laminar burning velocity data. The CEU-2022 mechanism (Wang et al., 2022) has the best overall performance, but it does not reproduce the experimental data satisfactorily under some conditions. A missing reaction step is identified in CEU-2022, and by inserting this reaction step and its rate parameters from the Alturaifi-2022 mechanism (Alturaifi et al., 2022) to CEU-2022, its performance improves significantly under the problematic conditions and also overall.

FC27

Pyrolysis and oxidation of HTPB polymer: experimental investigation and preliminary kinetic modeling

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Keywords: HTPB polymer, pyrolysis, combustion, kinetic modelling, solid propellants

This study investigates hydroxyl-terminated polybutadiene (HTPB)-based fuels which are critical for applications in energetics and propulsion emphasizing the decomposition of the polymer and the subsequent combustion of product gases. Additional experimental targets are acquired to drive kinetic model development on complex polymer mixtures. The objectives are to elucidate the behavior of HTPB in pyrolytic and oxidative environments and to develop predictive kinetic models describing the release of volatiles that are then ignited in the gas-phase in the targeted propulsion application.

Experimental investigations utilized thermogravimetric analysis (TGA) for quantitative analysis, delineating distinct regions of decomposition each characterized by proposed reaction classes. Chromatographic methods (GC/MS and μGC) were employed for TGA effluent gas chemical speciation. At moderate heating rates (60°C/min), the decomposition process exhibited two distinct regions: an initial devolatilization phase, characterized by the scission of urethane linkages and subsequent polymer depolymerization, followed by a plateau with near-zero net release of volatile compounds [1]. Higher heating rates (590 and 680°C/min) resulted in a single mass loss regime. In oxidative environments, polymer degradation exhibited higher apparent activation energies compared to inert conditions (i.e., 193.0 vs. 101.7 kJ/mol).

An existing chemical kinetic framework for the condensed phase pyrolysis of polymers [2] was preliminarily extended to describe polymer degradation. Successive coupling with secondary gas-phase subsets provides a foundational understanding of decomposition characteristics, product distribution and combustion characteristics such as ignition delay times, standoff distance between the polymer and the flame and detonation potential of produced gases.

This integrative approach leverages experimental and modeling techniques to provide a mechanistic understanding of HTPB-based fuel combustion under extreme conditions, thereby enhancing the predictive capabilities in practical applications.

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