

Markus Köhler, Patrick Oswald, Dominik Krueger, Ryan Whitside, Combustion Chemistry of Fuels: Quantitative Speciation Data Obtained from an Atmospheric High-temperature Flow Reactor with Coupled Molecular-beam Mass Spectrometer, J. Vis. Exp. 132 (2018) e56965.

The original publication is available at <https://www.jove.com/video/56965>

[[doi:10.3791/56965](https://doi.org/10.3791/56965)]

TITLE:

Combustion chemistry of fuels: Quantitative speciation data obtained from an atmospheric high-temperature flow reactor with coupled molecular-beam mass spectrometer

AUTHORS & AFFILIATIONS:

Köhler, Markus
Institute of Combustion Technology
German Aerospace Center (DLR)
Stuttgart, Germany
m.koehler@dlr.de

Oßwald, Patrick
Institute of Combustion Technology
German Aerospace Center (DLR)
Stuttgart, Germany
Patrick.osswald@dlr.de

Krüger, Dominik
Institute of Combustion Technology
German Aerospace Center (DLR)
Stuttgart, Germany
dominik.krueger@dlr.de

Whitside, Ryan
Institute of Combustion Technology
German Aerospace Center (DLR)
Stuttgart, Germany
R.whitside@hotmail.com

CORRESPONDING AUTHOR:

Dr. Markus Köhler
Email Address: m.koehler@dlr.de
Tel: +49 (711) 6862-756

KEYWORDS:

Molecular-beam mass spectrometry (MBMS), laminar flow reactor, speciation data, biofuels, jet fuel components, combustion chemistry, reaction kinetics, in situ speciation

SHORT ABSTRACT:

An investigation of the oxidative combustion chemistry of novel biofuels, fuel components, or jet fuels by comparison of quantitative speciation data is presented. The data can be used for kinetic model validation and enables fuel assessment strategies. This manuscript describes the atmospheric high-temperature flow reactor and demonstrates its capabilities.

LONG ABSTRACT:

This manuscript describes a high-temperature flow reactor experiment coupled to the powerful molecular beam mass spectrometry (MBMS) technique. This flexible tool offers a detailed observation of chemical gas-phase kinetics in reacting flows under well-controlled conditions. The vast range of operating conditions available in a laminar flow reactor enables access to extraordinary combustion applications that are typically not achievable by flame experiments. These include rich conditions at high temperatures relevant for gasification processes, the peroxy chemistry governing the low temperature oxidation regime or investigations of complex technical fuels. The presented setup allows measurements of quantitative speciation data for reaction model validation of combustion, gasification and pyrolysis processes, while enabling a systematic general understanding of the reaction chemistry. Validation of kinetic reaction models is generally performed by investigating combustion processes of pure compounds. The flow reactor has been enhanced to be suitable for technical fuels (e.g. multi-component mixtures like Jet A-1) to allow for phenomenological analysis of occurring combustion intermediates like soot precursors or pollutants. The controlled and comparable boundary conditions provided by the experimental design allow for predictions of pollutant formation tendencies. Cold reactants are fed premixed into the reactor that are highly diluted (around 99 vol% in Ar) in order to suppress self-sustaining combustion reactions. The laminar flowing reactant mixture passes through a known temperature field, while the gas composition is determined at the reactor's exhaust as a function of the oven temperature. The flow reactor is operated at atmospheric pressures with temperatures up to 1,800 K. The measurements themselves are performed by decreasing the temperature monotonically at a rate of -200 K/h. With the sensitive MBMS technique, detailed speciation data is acquired and quantified for almost all chemical species in the reactive process, including radical species.

INTRODUCTION:

Understanding combustion processes in the wake of modern, low-emission fuels from renewable resources is a challenge for today's societies' ecological and economic topics. They have the potential to reduce our dependence on fossil fuels, offset CO₂ emissions, and have a positive impact on harmful pollutant emissions such as soot and its toxic precursors¹. Combining this fast growing field with their utilization in modern combustor systems, the demand on a fundamental understanding of the governing chemical and physical processes has increased dramatically². Even today, the complex chemical reaction networks resulting from the radical chain reactions are still not fully understood. To analyze or even control phenomena like pollutant formation or (auto) ignition processes, the detailed knowledge of chemical reaction networks is a crucial piece of the puzzle³.

To investigate and understand those chemical reaction networks, experimental and numerical approaches are mandatory. Experimentally, the combustion chemistry is typically studied by applying experiments with simplified and well controlled flow environments to target specific questions. The high complexity and dynamics of individual sub processes prevent exact reproduction of the conditions of technical combustors by the fundamental experiments, while allowing the tracking of the designated key features such as temperature, pressure, heat release, or chemical species. Early on, the need for different experimental approaches became

apparent, each tackling a specific question and providing a subsequent set of information contributing to the overall global picture of the combustion chemistry. To cover the full range of conditions and gather those subsequent information sets to describe complex conditions occurring in technical systems various approaches were successfully developed. Well established techniques include:

- Shock tubes⁴⁻⁶ and rapid compression machines⁷. These devices provide high control of pressure and temperature over a wide range. However, the accessible reaction time and suitable analytical techniques are limited.
- Laminar premixed flames^{3,8-11} are ideal to gain high-temperature conditions in combination with a simple flow field. Since the spatial dimension of the reaction zone decreases with increasing pressure, premixed flames are typically investigated at low-pressure conditions for speciation purposes.
- Counterflow diffusion flames¹²⁻¹⁵ are ideal for investigating the flamelet regime in turbulent combustion. They mimic the strain due to inhomogeneities in a real turbulent flow, but are, again, highly limited in analytical speciation techniques.
- Various reactor experiments¹⁶⁻¹⁸ (static, stirred and plug-flow) provide access to high-pressure environments, while temperatures are typically lower compared to flame environments. Common approaches are:
 - Static reactors are widely used for e.g. pulse photolysis experiments, but are in general limited by long residence times and low temperatures.
 - Jet-stirred reactors, *i.e.* gas version of a perfectly stirred reactor (PSR), rely on the efficient mixing of the gas phase and can be operated at steady state with constant residence time, temperature and pressure, making it easy to model. However, molecules have time to migrate to the hot surfaces and undergo heterogeneous reactions.
 - Numerous flow reactor approaches are known, with the plug flow reactor (PFR) as one of the most popular approaches for describing chemical reactions in continuous, flowing systems of cylindrical geometry. Plug flow conditions at steady state are assumed with fixed residence time of the plug as a function of its position for ideal PFRs.

Complementary to those valuable techniques in the field of experimental combustion kinetics, a high-temperature laminar flow reactor experiment^{19,20} employing the molecular beam mass spectrometry (MBMS) technique for tracing species development in detail is presented^{21,22} herein. Laminar flow conditions, working at atmospheric pressure and accessible temperatures up to 1,800 K are the main characteristics of the flow reactor, while the sensitive MBMS technique allows the detection of almost all chemical species present in the combustion process. This includes highly reactive species such as radicals that are not or hardly traceable with other detection methods. The MBMS technique is widely used for the detailed investigation of reaction networks in flames of conventional and modern alternative fuels, such as alcohols or ethers²³⁻²⁵ and has demonstrated to be of great value for modern kinetic model development.

Figure 1 shows the schematic of the high-temperature flow reactor with a zoomed frame of the

sampling probe and two pictures highlighting the probe setup and the overall experiment. The system can be divided in two segments: first, the high-temperature flow reactor with gas supplies and vaporizer system and second, the MBMS time-of-flight detection system. In operation, the exit of the flow tube is mounted directly to the sampling nozzle of the MBMS system. The gas is sampled directly from the reactor outlet and transferred to the high-vacuum detection system. Here, ionization is performed by electron ionization with subsequent time-of-flight detection.

The reactor has a 40 mm inner diameter ceramic (Al_2O_3) pipe of 1,497 mm length placed in a high temperature oven (e.g., Gero, Type HTRH 40-1000). The total heated section is 1,000 mm in length. Gases are fed premixed and pre-vaporized into the reactor by a tempered flange (typically tempered to $\sim 80^\circ\text{C}$). The highly diluted (ca. 99 vol% in Ar), laminar flowing reactant mixture passes through a known temperature profile (details on temperature characterization will be given below). Detection of the gas composition takes place at the reactor outlet as a function of the oven temperature. Measurements are performed at constant inlet mass flow, while a monotonically decreasing temperature ramp (-200 K/h) is applied to the oven in the range of 1,800 K to 600 K. Note that similar results may be obtained when distinct temperatures are measured at isothermal oven temperatures and thermal inertia is considered properly. The thermal stabilization of the system still takes some time and the temperature ramp is selected as a compromise of averaging time for a (negligible) small temperature increment and total measurement time per series. The averaging time (45 s) of the MBMS corresponds to 2.5 K. The resulting residence times are around 2 s (at 1,000 K) for the given conditions. Finally, due to the temperature reproducibility, a relative precision of the measured temperatures of $\pm 5\text{ K}$ or better can be stated for the present reactor experiment.

Figure 2 shows the schematic of the vaporizing system, optimized to investigate even complex hydrocarbon mixtures such as technical jet fuels. All input streams are metered in high precision (accuracy $\pm 0.5\%$) by Coriolis mass flow meters. Vaporization of the fuel is realized by a commercial vaporizer system at temperatures up to 200°C . All supply lines with pre-vaporized fuels are preheated with temperatures of typically 150°C to prevent condensation of the liquid fuels, while avoiding thermal degradation at the same time. Complete and stable vaporization is routinely checked and may even occur at temperatures below the normal boiling point of the respective fuels. Complete evaporation was ensured by the small fuel fraction and the low partial pressure (typically below 100 Pa) needed.

The gases are sampled by a quartz cone at the centerline of the reactor exit at ambient pressures (around 960 hPa) as seen in more detail in the zoomed frame of **Figure 1**. The nozzle tip has a $50\ \mu\text{m}$ orifice, which is located roughly 30 mm inside the ceramic tube at the end of the reaction zone. Note, that the sampling location is fixed with respect to the inlet. Thermal expansion of the oven tube only takes place at the outlet, which is not mechanically connected to the sampling system resulting in a temperature independent length of the reaction segment. All reactions are immediately quenched due to the formation of a molecular beam, when gasses are expanded into high vacuum (two differential pumping stages; 10^{-2} and 10^{-4} Pa)^{25,26}. The sample is guided to the ion source of an electron impact (EI) time-of-flight (TOF) mass

spectrometer (e.g., Kaesdorf, mass resolution $R = 3,000$) capable of determining the exact mass of the present species in suitable precision to determine the elemental composition within a C/H/O system. The electron energy is set to low values (typically 9.5-10.5 eV) in order to minimize fragmentation due to the ionization process. Note that the diluent and reference species argon is still detectable due to the broad energy distribution of the ionizing electrons (1.4 eV FWHM). While Ar can be measured with good S/N, the low electron energy does not allow for sufficient determination of the major species (H_2O , CO_2 , CO , H_2 , O_2 , and fuel) profiles, which are present in significant lower concentrations.

In addition to the detection by TOF, a residual gas analyzer (RGA), *i.e.* a quadrupole mass spectrometer, is placed in the ionization chamber to monitor the six species above with a higher electron energy (70 eV) simultaneously to the MBMS-TOF measurements.

REPRESENTATIVE RESULTS:

A typical mass spectrum of the sampled gas composition is shown in **Figure 3**. With the given setup of a mass resolution of approx. 3,000, species up to $m/z = 260$ u can be detected within the C/H/O system. After a mass calibration procedure, the peaks are integrated for each mass-to-charge (m/z) ratio with deconvolution algorithms for evaluating under-resolved signals. After background and fragmentation corrections, the signal can be quantified using the appropriate calibration factors versus a reference species of known concentration (typically the inert gas argon). Several complex strategies for obtaining calibration factors are available including direct cold gas measurements (as shown), literature ionization cross sections or estimation procedures as well as internal calibration strategies. The appropriate choice depends on the individual species, the measurement conditions and the available data. For a detailed description on the applicable methods and strategies see references^{18,28-30}. The specific procedures for the flow reactor are available in the supplemental material of Ref. 22. The mole fraction is finally plotted against the average temperature of the corresponding 2.5 K interval, resulting in a typical mole fraction vs oven temperature plot shown in **Figure 3 (C)**.

To examine, understand and analyze complex reaction networks in combustion, detailed kinetic modeling has proven itself as a valuable complementary tool. The presented experimental method of a laminar flow reactor has demonstrated several times^{20,27} its validity as a basis for kinetic model development. A plug flow approximation (*i.e.* diffusion, axial as well as radial, is neglected and uniform radial velocity is assumed) of the laminar flow field has been shown to give a suitable representation of the experimental conditions. This approximation allows for direct transformation of the spatial position x to a distinct reaction (residence) time τ and a simple 0D consideration of species and temperature evolution as function of reaction time only can be applied. Therefore, the spatial temperature profile is used as an input parameter for the reactor model to obtain the spatial evolution of the participating species along the reactor axis. **Figure 4** shows the spatial mole fraction profiles of formaldehyde and acetylene for four selected oven temperatures obtained from a stoichiometric CH_4 measurement²¹. The kinetic model calculations are performed applying the plug flow reactor module of Chemical Work Bench (CWB). The approach allows for individual calculations for each oven temperature. Calculations are performed applying individual temperature profiles obtained from a scaling

law, as given in Ref. 22, based on experimental temperature measurements. The model results at the reactor exit are then plotted against the corresponding oven temperature for comparison to the experimental results. To demonstrate the typical capabilities of the modeling results, calculations are performed using the well validated USC-II mechanism³¹. As **Figure 4** indicates, there is an excellent agreement between the measured data and the kinetic model values for the main components (**Figure 4 (A)**) and the intermediates species (**Figure 4 (B)**).

Typical results for a single component investigation of oxidation processes, are shown in **Figure 5**. **Figure 5(A)** indicates the potential jet fuel compound p-menthane, featuring major species profiles, **Figure 5(B)** shows stoichiometric behavior, and **Figure 5(C)** the intermediate species. Results are obtained at ambient pressure and at stoichiometric ($\phi = 1.0$) conditions. The reaction sequence for major specie, *i.e.* reactants and products, gives a representative example for the structure typically observed at this type of flow reactor. The nominal inlet composition is measured until decay in the fuel mole fraction is observed at a certain temperature. The fuel is consumed and primarily converted to combustion intermediates. "Ignition" occurs when O_2 and the fuel exhibit their steepest reduction in concentration and CO_2 and H_2O exhibit their steepest increasing gradient. Under lean to stoichiometric conditions, this is also where the intermediate CO is rapidly consumed. Remember when using high dilutions in the given setup, no self-sustaining reactions occur or are repressed respectively. A full analysis of the stoichiometric variations, fuel decomposition pathways or even soot precursor formation can be performed by using data for the intermediate species; for the scope of this section, a lengthy discussion is omitted. The presented data can be used for the development of chemical reaction models.

Typically, validation of kinetic reaction models is performed by investigating combustion processes of pure compounds. As a next step in complexity, the flow-reactor setup can be used for technical fuels composed of multi-component mixtures such as jet fuels. **Figure 6(A)** shows major species profiles for stoichiometric ($\phi = 1.0$) and rich ($\phi = 1.5$) conditions. Profiles are similar to the ones shown earlier. However, the fuel decomposition curve is a combination of several single compounds showing a typical fuel decay behavior. The O_2 and fuel profiles both start at a maximum at low temperatures and are consumed as the reactor temperature increases. In-depth analysis in **Figure 6(B)** shows the major components found in the jet fuel and their individual consumption. In general, a similar decay can be observed for the hydrocarbon species. Interestingly, the aromatic species show the most deviation with a distinct plateau region before the steeper decay, which shifted to higher temperatures of around 1,000 K.

By enhancing the experiment to be used with technical fuels (e.g. multi-component mixtures), phenomenological analysis of occurring combustion intermediates like soot precursors or pollutants is possible. For this type of analysis, comparable conditions are mandatory. It was found beneficiary to have the same C/H conditions, requiring this value as an input parameter for the measurement design. The controlled and comparable boundary conditions enable predictions of pollutant formation tendencies as shown for soot precursors benzene or the propargyl radical in **Figure 7**. Both feature a typical intermediate profile shape with formation

and depletion during the reaction process. With reference to Jet A-1, a higher mole fraction for both species is measured for the cycloalkane p-methane, indicating a higher tendency to form pollutants in the combustion chemistry. This is quite interesting, since the propargyl radical has only a minor effect on the benzene formation in cyclohexane combustion³². Quite the opposite behavior is measured for the branched alkane farnesane with a lower mole fraction for both species compared to p-methane and the Jet A-1 reference fuel. In terms of soot formation resulting from combustion processes, a reducing effect on those pollutants is expected.

DISCUSSION:

The presented combination of an atmospheric high-temperature flow reactor with a molecular-beam mass spectrometry detection system enables quantitative speciation data for a range of operating conditions. Several studies^{21-23,27} demonstrated the flexibility of the experiment starting from rich methane conditions relevant for partial oxidation phenomena ($\phi = 2.5$), to investigating the combustion chemistry of modern jet fuel compounds like farnesane. Studies like these enable kinetic reaction modeling to cover more technical fields, e.g. the refined ethylene glycol mechanism suitable for technical gasification processes.

As shown above, the idea of a flow reactor design with in-situ diagnostics has been explored for decades and the method presented herein is nothing groundbreaking. However, with today's technical and experimental possibilities, this additional approach for current research areas is benefiting well-established strategies in combustion diagnostics.

Conclusively, the presented atmospheric flow reactor approach coupled with MBMS is a valuable addition to the established techniques in combustion chemistry (see Introduction). It shares, however, the same major drawback that is true for other methods as well: it is a very complex and sophisticated experimental setup. Designing a suitable MBMS detection system is a time-consuming, highly scientific demanding task and mastering the technique including careful, reliable quantification of the data takes time and effort. Note that no standard procedures are commercially available. However, designing a customized setup like this offers new and creative possibilities for modern scientific questions.

Crucial for a successful application and interpretation of the data is a careful characterization of the experiment and the choice of boundary conditions¹⁶. While the detection system is robust and flexible, the material for the flow tube may depend heavily on the experimental conditions. The presented ceramic tube has been proven successful for most applications, while investigations focusing on particles and larger soot precursors indicated unexpected results and unwanted side effects in the mass spectra. Changing the material to quartz has shown a vast improvement in particle measurements; however, investigations are limited to distinct temperature regimes below 1,400 K. Note that recent test runs have shown no influence on the gas phase detection.

Following on the challenging hardware setup, the careful characterization of the experimental behavior and especially the temperature field is mandatory for data evaluation and interpretation. Results can only be modelled reasonably if the respective temperature profile is

known for each condition. Issues such as wall/gas phase interaction, flow properties, invasive probing and carrier gas were carefully investigated. Taking all of these aspects into account, several modelling approaches have demonstrated the capability and validity of the method successfully and underlined the valuable addition to kinetic model development.

The possible applications mentioned here are a starting point and future contributions have to be further explored as well as current limitations pushed to the extreme. One major limitation so far is the mass resolution of the detection instrument. While a mass resolution of $\Delta m = 3,000$ is sufficient for most combustion species, isomeric species cannot be separated or identified. Highly advanced experiments like synchrotron based approaches^{28,33-38} or generic theoretical studies on reaction kinetics are needed in the future to provide more detailed knowledge and improve upon the identification capabilities.

The rapid evolution from simple methane to complex technical jet-fuels covers a broad range of accessible compounds. Currently, the major focus is on liquid single components and complex mixtures for technical applications such as jet fuels. As a next level in evolution, the boundary conditions like temperature, flow properties and pressure could be a target and multidimensional aspects are worth investigating³⁹ more than ever. Even so, the temperature already covers a range from low-temperature (around 800 K) combustion to pyrolysis (2100 K). Higher pressures would be useful for targeting technical conditions and model development, where speciation data is generally rare in literature. With modern materials and availabilities, new experimental designs for speciation data obtained by a high-pressure, high-temperature flow reactor is within reach.

ACKNOWLEDGMENTS:

The experiments were carried out in the mass spectrometry department at the Institute of Combustion Technology, Deutsches Zentrum für Luft- und Raumfahrt (DLR) in Stuttgart, Germany. The work was also supported by the Helmholtz Energy-Alliance “Synthetic Liquid Hydrocarbons”, the Center-of-Excellence “Alternative Fuels” and the DLR project “Future Fuels”. The authors wish to thank Patrick Le Clercq and Uwe Riedel for fruitful discussions on jet fuels and Ryan Whitside for pioneering experiences with the experimental setup.

DISCLOSURES:

The authors have nothing to disclose.

REFERENCES:

- 1 Moore, R. H. *et al.* Biofuel blending reduces particle emissions from aircraft engines at cruise conditions. *Nature*. **543** (7645), 411-415, doi:10.1038/nature21420, (2017).
- 2 Braun-Unkloff, M., Kathrotia, T., Rauch, B. & Riedel, U. About the interaction between composition and performance of alternative jet fuels. *CEAS Aeronautical Journal*. **7** (1), 83-94, doi:10.1007/s13272-015-0178-8, (2016).
- 3 Egolfopoulos, F. N. *et al.* Advances and challenges in laminar flame experiments and implications for combustion chemistry. *Prog Energ Combust*. **43** 36-67,

- doi:[10.1016/j.pecs.2014.04.004](https://doi.org/10.1016/j.pecs.2014.04.004), (2014).
- 4 Lynch, P. T., Troy, T. P., Ahmed, M. and Tranter, R. S. Probing combustion chemistry in a miniature shock tube with synchrotron VUV photo ionization mass spectrometry. *Anal Chem.* **87** (4), 2345-2352, doi:[10.1021/ac5041633](https://doi.org/10.1021/ac5041633), (2015).
 - 5 Pelucchi, M. *et al.* An experimental and kinetic modeling study of the pyrolysis and oxidation of n-C₃C₅ aldehydes in shock tubes. *Combust. Flame.* **162** (2), 265-286, doi:[10.1016/j.combustflame.2014.07.027](https://doi.org/10.1016/j.combustflame.2014.07.027), (2015).
 - 6 Hanson, R. K. & Davidson, D. F. Recent advances in laser absorption and shock tube methods for studies of combustion chemistry. *Prog Energ Combust.* **44** 103-114, doi:[10.1016/j.pecs.2014.05.001](https://doi.org/10.1016/j.pecs.2014.05.001), (2014).
 - 7 Sung, C.-J. and Curran, H. J. Using rapid compression machines for chemical kinetics studies. *Prog Energ Combust.* **44** 1-18, doi:[10.1016/j.pecs.2014.04.001](https://doi.org/10.1016/j.pecs.2014.04.001), (2014).
 - 8 Kohse-Höinghaus, K. *et al.* Cover Picture: Biofuel Combustion Chemistry: From Ethanol to Biodiesel (Angew. Chem. Int. Ed. 21/2010). *Angw Chem Int Edit.* **49** (21), 3545-3545, doi:[10.1002/anie.201001648](https://doi.org/10.1002/anie.201001648), (2010).
 - 9 Köhler, M. *et al.* 1-, 2- and 3-Pentanol combustion in laminar hydrogen flames – A comparative experimental and modeling study. *Combust. Flame.* **162** (9), 3197-3209, doi:[10.1016/j.combustflame.2015.05.007](https://doi.org/10.1016/j.combustflame.2015.05.007), (2015).
 - 10 Li, Y. *et al.* Experimental Study of a Fuel-Rich Premixed Toluene Flame at Low Pressure. *Energ Fuel.* **23** (3), 1473-1485, doi:[10.1021/ef800902t](https://doi.org/10.1021/ef800902t), (2009).
 - 11 Yang, B. *et al.* Identification of combustion intermediates in isomeric fuel-rich premixed butanol–oxygen flames at low pressure. *Combust. Flame.* **148** (4), 198-209, doi:[10.1016/j.combustflame.2006.12.001](https://doi.org/10.1016/j.combustflame.2006.12.001), (2007).
 - 12 Reuter, C. B, Won, S. H. and Ju, Y. Flame structure and ignition limit of partially premixed cool flames in a counterflow burner. *P Combust Inst.* **36** (1), 1513-1522, doi:[10.1016/j.proci.2016.06.067](https://doi.org/10.1016/j.proci.2016.06.067), (2017).
 - 13 Reuter, C. B. *et al.* Experimental study of the dynamics and structure of self-sustaining premixed cool flames using a counterflow burner. *Combust. Flame.* **166** 125-132, doi:[10.1016/j.combustflame.2016.01.008](https://doi.org/10.1016/j.combustflame.2016.01.008), (2016).
 - 14 Bufferand, H., Tosatto, L., La Mantia, B., Smooke, M. D. and Gomez, A.. A. Experimental and computational study of methane counterflow diffusion flames perturbed by trace amounts of either jet fuel or a 6-component surrogate under non-sooting conditions. *Combust. Flame.* **156** (8), 1594-1603, doi:[10.1016/j.combustflame.2009.03.006](https://doi.org/10.1016/j.combustflame.2009.03.006), (2009).
 - 15 Lefkowitz, J. K. *et al.* A chemical kinetic study of tertiary-butanol in a flow reactor and a counterflow diffusion flame. *Combust. Flame.* **159** (3), 968-978, doi:[10.1016/j.combustflame.2011.10.004](https://doi.org/10.1016/j.combustflame.2011.10.004), (2012).
 - 16 Dryer, F. L., Haas, F. M., Santner, J., Farouk, T. I. and Chaos, M. Interpreting chemical kinetics from complex reaction–advection–diffusion systems: Modeling of flow reactors and related experiments. *Prog Energ Combust.* **44** 19-39, doi:[10.1016/j.pecs.2014.04.002](https://doi.org/10.1016/j.pecs.2014.04.002), (2014).
 - 17 Zhao, H., Yang, X. and Ju, Y. Kinetic studies of ozone assisted low temperature oxidation of dimethyl ether in a flow reactor using molecular-beam mass spectrometry. *Combust. Flame.* **173** 187-194, doi:[10.1016/j.combustflame.2016.08.008](https://doi.org/10.1016/j.combustflame.2016.08.008), (2016).
 - 18 Oßwald, P. *et al.* Combustion of butanol isomers – A detailed molecular beam mass

- spectrometry investigation of their flame chemistry. *Combust. Flame.* **158** (1), 2-15, doi:10.1016/j.combustflame.2010.06.003, (2011).
- 19 Herrmann, F., Oßwald, P. and Kohse-Höinghaus, K. Mass spectrometric investigation of the low-temperature dimethyl ether oxidation in an atmospheric pressure laminar flow reactor. *P Combust Inst.* **34** (1), 771-778, doi:10.1016/j.proci.2012.06.136, (2013).
- 20 Li, Y. *et al.* Experimental and kinetic modeling study of tetralin pyrolysis at low pressure. *P Combust Inst.* **34** (1), 1739-1748, doi:[10.1016/j.proci.2012.05.002](https://doi.org/10.1016/j.proci.2012.05.002), (2013).
- 21 Oßwald, P. and Köhler, M. An atmospheric pressure high-temperature laminar flow reactor for investigation of combustion and related gas phase reaction systems. *Rev Sci Instrum.* **86** (10), 105109, doi:[10.1063/1.4932608](https://doi.org/10.1063/1.4932608), (2015).
- 22 Oßwald, P., Whitside, R., Schäffer, J. and Köhler, M. An experimental flow reactor study of the combustion kinetics of terpenoid jet fuel compounds: Farnesane, p-menthane and p-cymene. *Fuel.* **187** 43-50, doi:[10.1016/j.fuel.2016.09.035](https://doi.org/10.1016/j.fuel.2016.09.035), (2017).
- 23 Kathrotia, T., Naumann, C., Oßwald, P., Köhler, M. and Riedel, U. Kinetics of Ethylene Glycol: The first validated reaction scheme and first measurements of ignition delay times and speciation data. *Combust. Flame.* **179** 172-184, doi:[10.1016/j.combustflame.2017.01.018](https://doi.org/10.1016/j.combustflame.2017.01.018), (2017).
- 24 Hansen, N., Cool, T. A., Westmoreland, P. R. and Kohse-Höinghaus, K. Recent contributions of flame-sampling molecular-beam mass spectrometry to a fundamental understanding of combustion chemistry. *Prog Energ Combust.* **35** (2), 168-191, doi:[10.1016/j.pecs.2008.10.001](https://doi.org/10.1016/j.pecs.2008.10.001), (2009).
- 25 Qi, F. Combustion chemistry probed by synchrotron VUV photoionization mass spectrometry. *P Combust Inst.* **34** (1), 33-63, doi:10.1016/j.proci.2012.09.002, (2013).
- 26 Biordi, J. C. Molecular beam mass spectrometry for studying the fundamental chemistry of flames. *Prog Energ Combust.* **3** (3), 151-173, doi:10.1016/0360-1285(77)90002-8, (1977).
- 27 Köhler, M. *et al.* Speciation data for fuel-rich methane oxy-combustion and reforming under prototypical partial oxidation conditions. *Chem Eng Sci.* **139** 249-260, doi:[10.1016/j.ces.2015.09.033](https://doi.org/10.1016/j.ces.2015.09.033), (2016).
- 28 Oßwald, P. *et al.* In situ flame chemistry tracing by imaging photoelectron photoion coincidence spectroscopy. *Rev Sci Instrum.* **85** (2), 025101, doi:[10.1063/1.4861175](https://doi.org/10.1063/1.4861175), (2014).
- 29 Oßwald, P. *et al.* Combustion Chemistry of the Butane Isomers in Premixed Low-Pressure Flames. *Zeitschrift für Physikalische Chemie.* Vol. 225 1029 (2011).
- 30 Schenk, M. *et al.* Detailed mass spectrometric and modeling study of isomeric butene flames. *Combust. Flame.* **160** (3), 487-503, doi:10.1016/j.combustflame.2012.10.023, (2013).
- 31 Wang, H. *et al.* USC Mech Version II. High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds, http://ignis.usc.edu/USC_Mech_II.htm. (2007).
- 32 Li, W. *et al.* Multiple benzene-formation paths in a fuel-rich cyclohexane flame. *Combust. Flame.* **158** (11), 2077-2089, doi:[10.1016/j.combustflame.2011.03.014](https://doi.org/10.1016/j.combustflame.2011.03.014), (2011).
- 33 Bierkandt, T., Hemberger, P., Osswald, P., Köhler, M. and Kasper, T. Insights in m-xylene decomposition under fuel-rich conditions by imaging photoelectron photoion coincidence spectroscopy. *P Combust Inst.* **36** (1), 1223-1232,

- doi:10.1016/j.proci.2016.06.143, (2017).
- 34 Taatjes, C. A. *et al.* Enols Are Common Intermediates in Hydrocarbon Oxidation. *Science*. **308** (5730), 1887-1889, doi:10.1126/science.1112532, (2005).
- 35 Li, Y. *et al.* An experimental study of the rich premixed ethylbenzene flame at low pressure. *P Combust Inst.* **32** (1), 647-655, doi:[10.1016/j.proci.2008.05.025](https://doi.org/10.1016/j.proci.2008.05.025), (2009).
- 36 Yuan, W. *et al.* A comprehensive experimental and kinetic modeling study of ethylbenzene combustion. *Combust. Flame.* **166** 255-265, doi:[10.1016/j.combustflame.2016.01.026](https://doi.org/10.1016/j.combustflame.2016.01.026), (2016).
- 37 Hansen, N., Skeen, S. A., Michelsen, H. A., Wilson, K. R. and Kohse-Hoinghaus, K. Flame experiments at the advanced light source: new insights into soot formation processes. *J Vis Exp.* **87** (87), e51369, doi:10.3791/51369, (2014).
- 38 Qi, F. *et al.* Isomeric identification of polycyclic aromatic hydrocarbons formed in combustion with tunable vacuum ultraviolet photoionization. *Rev Sci Instrum.* **77** (8), 084101, doi:10.1063/1.2234855, (2006).
- 39 Hansen, N. *et al.* 2D-imaging of sampling-probe perturbations in laminar premixed flames using Kr X-ray fluorescence. *Combust. Flame.* **181** 214-224, doi:[10.1016/j.combustflame.2017.03.024](https://doi.org/10.1016/j.combustflame.2017.03.024), (2017).

FIGURE AND TABLE LEGENDS:

Figure 1: Schematic DLR high-temperature flow reactor with photographs. The zoomed cutout shows a detailed view of the sampling interface and the ionization source separated by the gate valve (A). Note that the high-temperature oven is mounted on moveable rails and sampling is performed inside the tube at ambient pressure (B). A picture of the quartz nozzle and skimmer is shown (C). Adopted from^{21,27}.

Figure 2: Fuel Vaporizer system. Schematic of the vaporizer system for liquid fuels and single compounds with commercial setup²² to the flow reactor setup inlet.

Figure 3: Typical raw signal provided by the MBMS system (A). The given mass resolution allows for the separation of species (B) and integration for further quantification. Plotting the mole fractions versus the oven temperature gives typical results for the laminar flow-reactor (C).

Figure 4: Kinetic modeling of stoichiometric methane oxidation using the USC-II mechanism³¹. Spatial model result (lines) for mole model fraction profiles of acetylene (C_2H_2) and formaldehyde (CH_2O) for at selected oven temperatures and the respective temperature profiles (A). Comparison to the experimental results (symbols) of intermediate (B) and major species (C), when temperature ramps are considered. Updated from Ref. 21.

Figure 5: Typical results for a single component investigation of oxidation processes. The main species profiles (A) for a potential jet fuel compound p-methane and comparison of the stoichiometric behavior (B). Selected intermediate species are shown (C) to gain information regarding reaction networks²².

Figure 6: Speciation data for Jet A-1 investigation. Main species (A) and fuel component mole fractions depletion (B) are shown as a function of the reactor temperature. Fuel components are consumed with higher temperatures.

Figure 7: In-depth soot precursor chemistry. Comparison of soot precursor intermediate benzene C_6H_6 (A) and the propargyl radical C_3H_3 (B) for p-methane and farnesane with reference to Jet A-1²². In both cases, p-Menthane shows a higher mole fraction compared to Jet A-1, while Farnesane features a lower mole fractions indicating a reduced tendency in forming soot precursors.

Figure 1: Schematic DLR high-temperature flow reactor with photographs. The zoomed cutout shows a detailed view of the sampling interface and the ionization source separated by the gate valve (A). Note that the high-temperature oven is mounted on moveable rails and sampling is performed inside the tube at ambient pressure (B). A picture of the quartz nozzle and skimmer is shown (C). Adopted from^{21,27}.

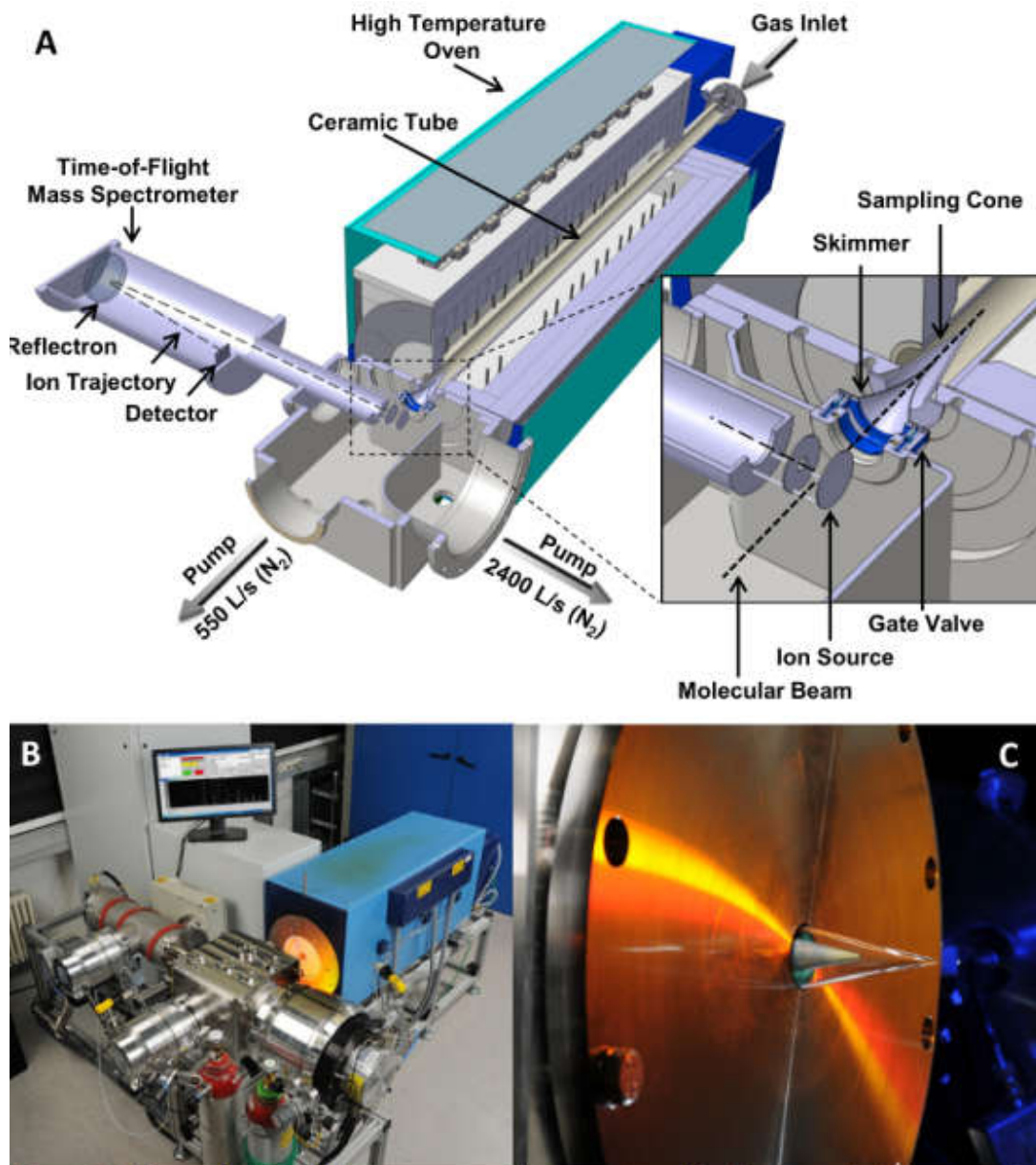


Figure 2: Fuel Vaporizer system. Schematic of the vaporizer system for liquid fuels and single compounds with commercial setup²² to the flow reactor setup inlet.

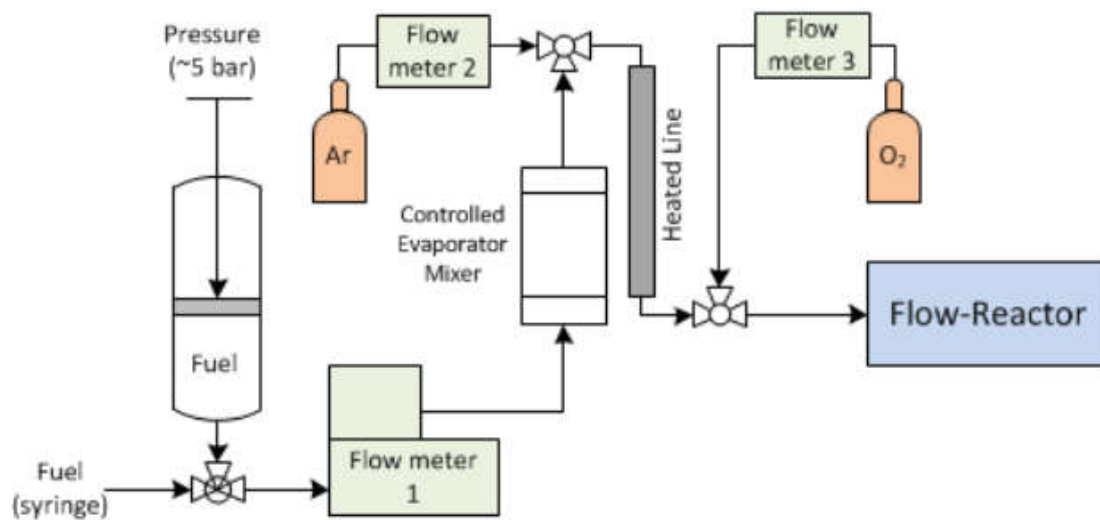


Figure 3: Typical raw signal provided by the MBMS system (A). The given mass resolution allows for the separation of species (B) and integration for further quantification. Plotting the mole fractions versus the oven temperature gives typical results for the laminar flow-reactor (C).

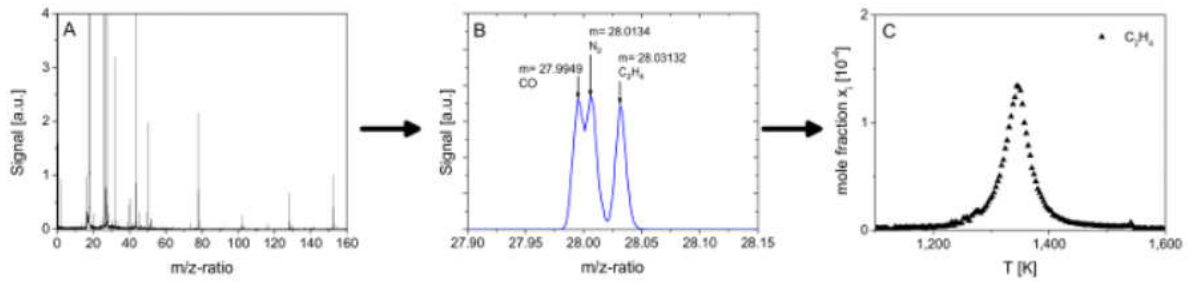


Figure 4: Kinetic modeling of stoichiometric methane oxidation using the USC-II mechanism³¹. Spatial model result (lines) for mole model fraction profiles of acetylene (C_2H_2) and formaldehyde (CH_2O) for at selected oven temperatures and the respective temperature profiles (A). Comparison to the experimental results (symbols) of intermediate (B) and major species (C), when temperature ramps are considered. Updated from Ref. 21.

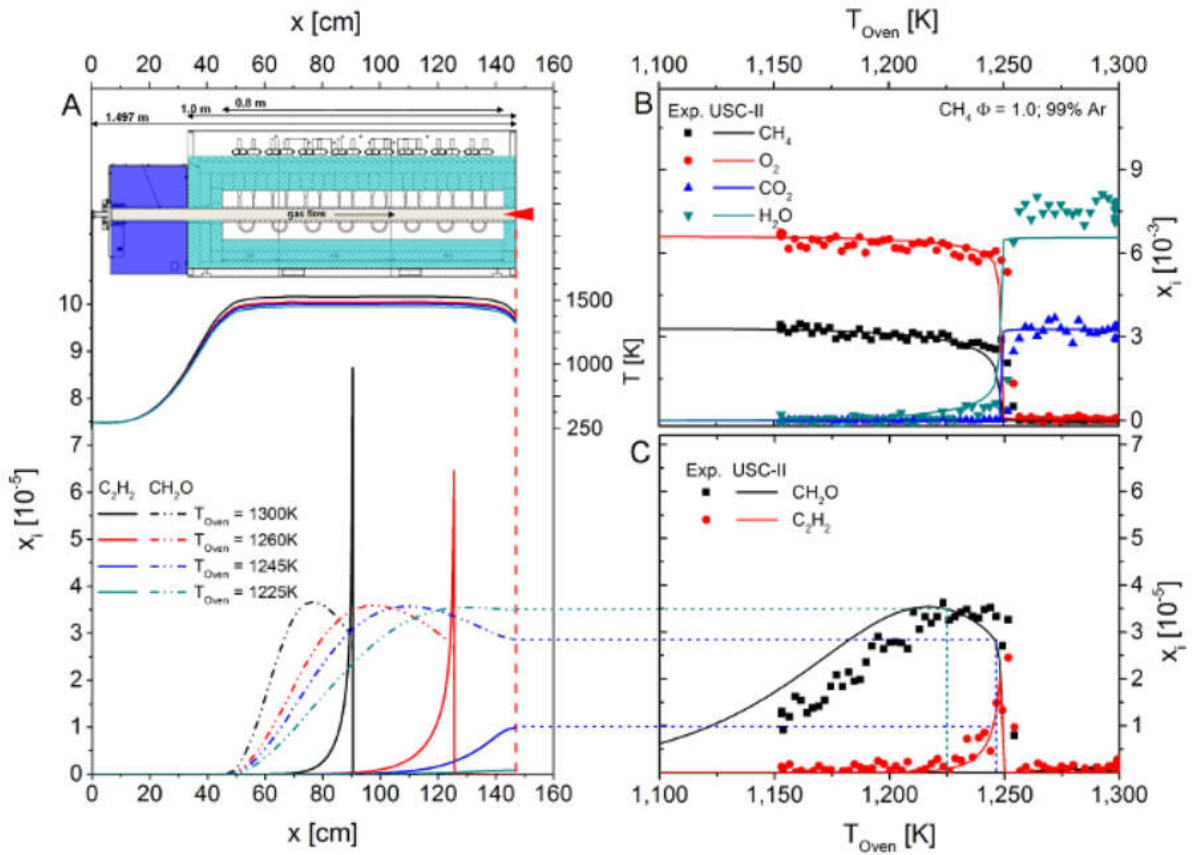


Figure 5: Typical results for a single component investigation of oxidation processes. The main species profiles (A) for a potential jet fuel compound p-methane and comparison of the stoichiometric behavior (B). Selected intermediate species are shown (C) to gain information regarding reaction networks²².

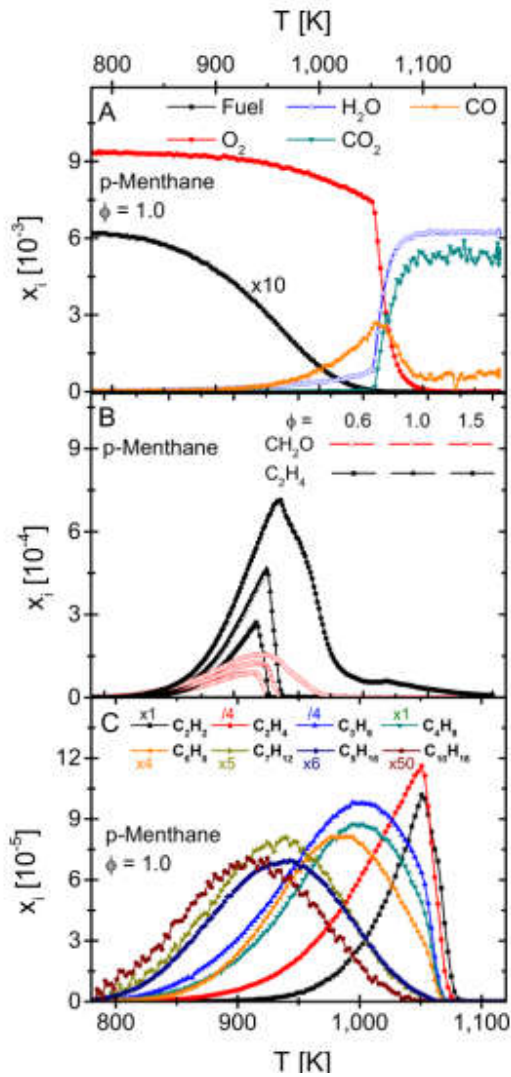


Figure 6: Speciation data for Jet A-1 investigation. Main species (A) and fuel component mole fractions depletion (B) are shown as a function of the reactor temperature. Fuel components are consumed with higher temperatures.

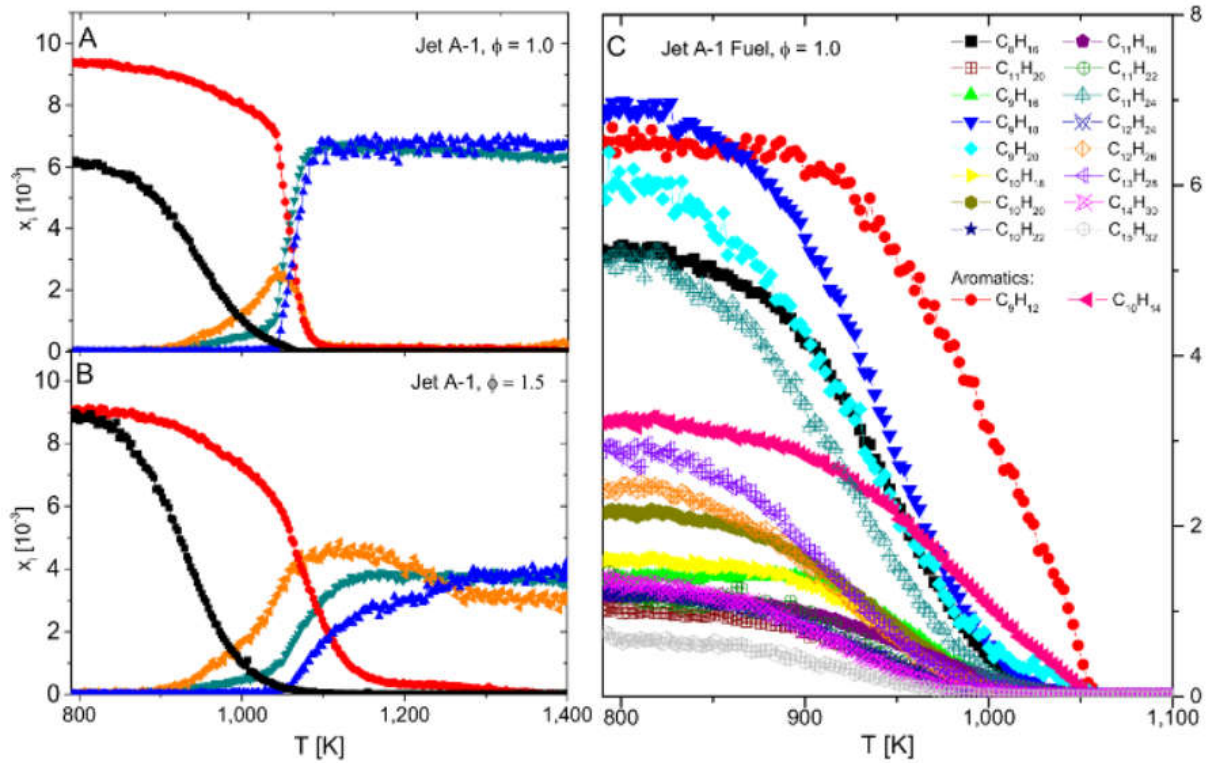
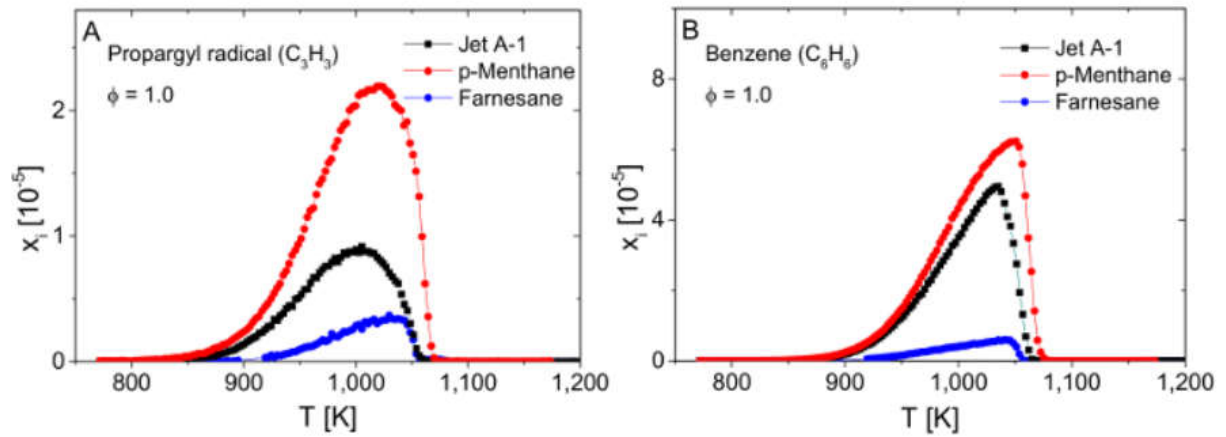


Figure 7: In-depth soot precursor chemistry. Comparison of soot precursor intermediate benzene C_6H_6 **(A)** and the propargyl radical C_3H_3 **(B)** for p-methane and farnesane with reference to Jet A-1²². In both cases, p-Menthane shows a higher mole fraction compared to Jet A-1, while Farnesane features a lower mole fractions indicating a reduced tendency in forming soot precursors.



PROTOCOL:

1. Setup of the molecular beam mass spectrometer (MBMS) and flow reactor system

- 1.1 Heat oven to designated start temperature, which is the highest temperature in designated measurement series. For typical conditions of Jet A-1 with $\Phi=1$, total oxidation is observed below 850 °C (~1,100 K). The choice of proper starting temperatures depends on the chemical nature of the investigated fuel and the stoichiometry (Φ).
- 1.2 Prepare Time-of-Flight (TOF) spectrometer for intermediate species detection. The TOF spectrometer is aligned to the molecular beam and thus provides reliable detection of labile species. The mass resolution is suitable for the determination of the elemental composition in a C/H/O system. To avoid fragmentation, soft ionization conditions are chosen. Values of typically 9.5 to 10.5 eV have been proven suitable for a typical investigation of combustion intermediates.
- 1.3 Prepare quadrupole spectrometer for major species detection. The quadrupole spectrometer (also called Residual Gas Analyzer, RGA) is placed inside the ionization chamber of the MBMS system nearby the molecular beam. Thus, just wall-scattered background gases are measured. However, since major species are stable, the background pressure well reflects their concentration at the sampling tip. For better signal-to-noise ratio, a high ionization energy of 70 eV may be chosen in this case.

2. Preparation of the fuel sample

- 2.1 Prepare the metal syringe for fuel supply.

Caution: Use proper personal protective equipment for fuel handling.

- 2.1.1 Fill 30 mL of the fuel sample to the vaporizers metal syringe.
- 2.1.2 Pressurize fuel supply system (metal syringe) up to 5 bar by adding pressurized air to the system though opening the valve.
- 2.1.3 Vent fuel lines and Coriolis mass flow meter by opening the valves in the fuel supply lines.
- 2.2 Heat up the vaporizer and gas supply lines: In the given setup, temperatures far below the normal pressure boiling point can be applied due to the high dilution. Ensure that the vapor pressure at the designated temperature of the highest boiling compound of the fuel is higher than its partial pressure in the gas stream. Typically, 200 °C is

adequate for Jet A-1.

- 2.3 Note that the coldest spot in the system is the tempered inlet flange to the oven. Make sure the diluted fuel cannot recondense at this spot. For typical Jet A-1 (99% dilution) setting the water cooling system to 80 °C is adequate.

3. Measurement and data acquisition

- 3.1 Place oven to the sampling position. The sampling cone must be placed inside the oven's ceramic tube. In the present experiment, the sampling location is close to the plateau value of the spatial temperature profile of the oven.

Note: The picture in **Figure 1** shows the cone and the reactor. The heated reactor (orange) is moved on rails towards the quartz cone.

- 3.2 Start diluent of choice by adding gas through the Coriolis mass flow meter. The mass flow meters are controlled by the original software package. Here, mass flow values can be set. Typically, 99% argon is used. In general, for liquid fuels, the diluent flow may be split to vaporizer and oxidizer gas streams by using an additional Cori mass flow meter parallel to Cori Flow 2 passing the heated line and connected directly to the oxidizer stream from Cori Flow 3.

- 3.3 Start continuous data recording (TOF and Quadrupole) by using the designated instrumental software.

Note: Start-Button clicked in Quadrupole software. Start button clicked in TOF software.

- 3.3.1 Add oxidizer O₂ by setting the value of 39.4 mg/min in the Coriolis flow meter software. Observe the incoming oxidizer as new peak in mass spectrum.

- 3.4 Add fuel by setting the appropriate flow condition of the Coriolis mass flow meter.

- 3.4.1 Check spectra: if complete oxidation in case of lean and stoichiometric conditions is achieved, a stable CO₂ mass signal is observable.

- 3.5 When signal intensities are stable for 4 to 5 measurements, a stabilization period ends. After the stabilization period, apply the continuous temperature decay ramp of typically -200 K/h to the oven. This leads to typical measurement times of 2 h per measurement run.

- 3.5.1 At a specific oven temperature during the ramp, observe a rapid change of the mass spectra. Sole combustion products (H₂O, CO₂ and CO, H₂ in rich cases) start to disappear and small combustion intermediates become detectable.

Note: With further decreasing temperature, visible intermediates become larger and larger. At cold oven temperatures, only the signal of fuel compounds and oxygen can be observed; no reactions are taking place within the present residence time of the reactor.

- 3.6 When the final temperature is stabilized (typically 500 °C; 10 min), switch off the oxidizer.
- 3.6.1 Continue recording measurements. Fuel characterization (composition of fragmentation) measurements can be obtained at conditions without oxidizer.
- 3.7 Switch off fuel in the Coriolis mass flow meter software by setting the value to 0. Data will be still recorded; these spectra can be used for background measurement.
- 3.8 Stop data recording by clicking the stop button in the software.

4 Calibration measurements

- 4.1 For calibration issues, mount a closed chamber in front of the sampling cone.

Note: The closed chamber is a tube, which is placed in front of the nozzle by hand.

- 4.2 Open valve to pump. The chamber is evacuated. Note that the vacuum is only needed to hold the chamber stable in front of the nozzle.
- 4.3 Apply binary mixtures (hydrocarbon of interest and Ar) or commercial calibration gasses for calibration. For demonstration, a customized gas mixture with CO and CO₂ and argon is used here.
- 4.4 Adjust the pressure in the calibration chamber by a needle valve to obtain signal intensity above the signal-to-noise ratio and below the saturation limit.
- 4.5 Start calibration measurements by starting data recording as performed for the individual measurement in 3.5 by clicking the start button in the TOF software.

5 Data processing

- 5.1 Sort the recorded signals based on the oven temperature they have been collected at.
- 5.2 At each recorded temperature, for each chosen species, calculate its mole fraction from the corresponding signal. Plot the mole fraction profiles vs. oven temperature (**Figure 3**).