

## Advances and Developments in Combustion Chemistry and Diagnostics.

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### Highlights

- Inspecting combustion chemistry: how to analyze reactive systems?
- Identifying potential pollutants: is fuel structure related to expected emissions?
- Modeling combustion chemistry: how to transfer laboratory results to practical systems?
- Beyond combustion: are these approaches also useful elsewhere?

### 1. Introduction

For future use of combustion energy for transportation, power generation and industrial processes, a decrease of both carbon footprint and pollutant emissions is mandatory. Such solutions need an interdisciplinary systems approach, with combustion chemistry and diagnostics as important ingredients [1]. With the introduction of alternative fuels, including second-generation biofuels derived from cellulosic biomass, new demands arise in reaction engineering, regarding sustainable fuel production as well as their combustion reactions [2]. These latter reactions are not only key to release the needed energy, but they also give rise to the exhaust composition including regulated or other hazardous compounds. Detailed reaction mechanisms that can describe ignition and oxidation of conventional and alternative fuels and their mixtures for different reaction conditions provide a physico-chemically well-founded basis to transfer the knowledge on fuel-structure-related molecular reactions into a practical environment. If suitably validated by experiments, they can enable prediction of combustion efficiency and pollutant formation. Combustion diagnostics offers a wide array of methods for laboratory and practical systems for this purpose [3-5] that can also be employed beyond combustion investigations. Here we will provide some examples of recent collaborative laboratory studies on the oxidation of various hydrocarbon and oxygenated fuels, mainly with a focus on the fuel-structure-specific reaction pathways leading to the formation of potential toxic combustion byproducts [6-10].

### 2. Methods

The in-situ analysis of the combustion chemistry in the present report has been performed in laboratory reactors and flames. While non-invasive, fast, high-repetition laser techniques are well suited to interrogate practical combustion systems [3], the universal nature of flame-sampling mass spectrometry permits the sensitive detection of a large number of stable and reactive intermediate species, including radicals [4,5]. Variants of this technique have been applied at low and intermediate temperatures in jet-stirred and flow reactors [6,7], in shock tubes, rapid compression machines, and in premixed and non-premixed flames [8-10]. Molecular-beam mass spectrometry with electron ionization or synchrotron-based single-photon ionization has been complemented with gas chromatography to detect gaseous species. Some advanced techniques such as photoelectron photoion coincidence spectroscopy [11], microwave spectroscopy [12] and methods to detect nascent soot particles [13] hold promise to extend the diagnostics toolbox.

### 3. Results and discussion

Combustion reaction model development and validation is much more mature for conventional hydrocarbon fuels under high-temperature premixed flame conditions than for some other domains of practical interest [14]. Areas that need improvement include consistent and systematically developed mechanisms for non-hydrocarbon fuel classes, a deeper understanding of soot nucleation, of fuel-specific autoignition reactions, of interactive effects in hydrocarbon/biofuel mixtures, of combustion at high pressure and related diagnostics to experimentally detect and measure key species and parameters of such reaction systems [1]. Substantial contributions may demand experiment, theory and model development to work hand-in-hand and to address

a large parameter range, involving often multi-center collaborations. Examples here will analyze reaction pathways and pollutant formation particularly for some ethers [15], ketones [8] and furan derivatives [6]. We will also show the influence of mixture effects on pollutant formation for some C<sub>4</sub>- and C<sub>5</sub>-fuels, especially in the fuel-rich regime and in hydrocarbon-oxygenate systems [9,16]. Also, experimental information regarding the formation of small aromatic ring compounds that are commonly assumed to precede soot nucleation will be discussed with an emphasis on the fuel structure, and the detection of nanometer-sized incipient soot particles will be briefly highlighted [10,13]. While experimental results on numerous flame and reactor conditions are becoming available, challenges of the techniques including sampling effects, lacking information on isomer/conformer structures and ionization cross sections, uncertainties for radical detection and of temperature measurements should be addressed with similar caution as shortcomings of present models. Only by joint efforts across the reaction kinetic, theoretical chemistry, modeling, chemical and mechanical engineering communities will reliable models of predictive capability emerge that can be used under current and future combustion conditions to assess the respective pollutant emission potential.

#### 4. Conclusions

Investigating the detailed oxidation chemistry of conventional and alternative fuels and fuel combinations with advanced diagnostics is one element in understanding the source of regulated and unregulated pollutants from combustion processes. Such knowledge is useful to construct and validate models that can then be properly reduced for engineering applications. Procedures such as used in combustion can be beneficially transferred to other systems, potentially including efficient industrial processes and coupling of the energy, transportation and production sectors.

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#### Keywords

(Bio-)fuel; pollutant emission; combustion; mass spectrometry.