FORMATION OF OXYGENATED POLYCYCLIC AROMATIC COMPOUNDS IN FLAME

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic materials. Their chemical and physical characteristics strongly influence their fate, transport in the environment and the way they interact with biological systems.

As today, there is no accurate predictive model for the formation and growth of PAHs. The aim of this study is to identify reaction pathways for the formation of PAHs using a unique computational tool based on stochastic discrete modeling, that describes the chemical pathways as function of reactive sites rather than fixed species. In this way the system can determine new species and pathways as time evolves. Using a counterflow flame as combustion environment, we show the formation of cyclic compounds with oxygen embedded, especially in high temperature regions. These oxy-PAHs represent a new class of compounds, whose chemistry needs to be included into current kinetic models [*Johansson et al., PNAS, 2016*]. Modeling results are validated with available experimental data in terms of mass spectra measured at different locations in the flame.

HYPOTHESIS

Oxygenated polycyclic aromatic compounds are formed in flames of hydrocarbons.

METHODOLOGY

Computational approach:

- 3-D computational fluid dynamics (CFD) simulations using the software CONVERGE [*Richards et. al., 2015*]
- Stochastic discrete modeling to explore the formation pathways of polycyclic aromatic compounds in flame using the Stochastic Nanoparticle Simulator (SNapS2) [*Wang et. al., in preparation*]. Given a set of chemical reactions and environmental conditions, SNapS2 simulates the trajectories of sequential reactions of a single particle. The analysis of a large ensemble of trajectories can give general insights into the growth process. The Snaps2 code is employed to compute the evolution of PAHs along the streamlines identified by the CFD simulations.

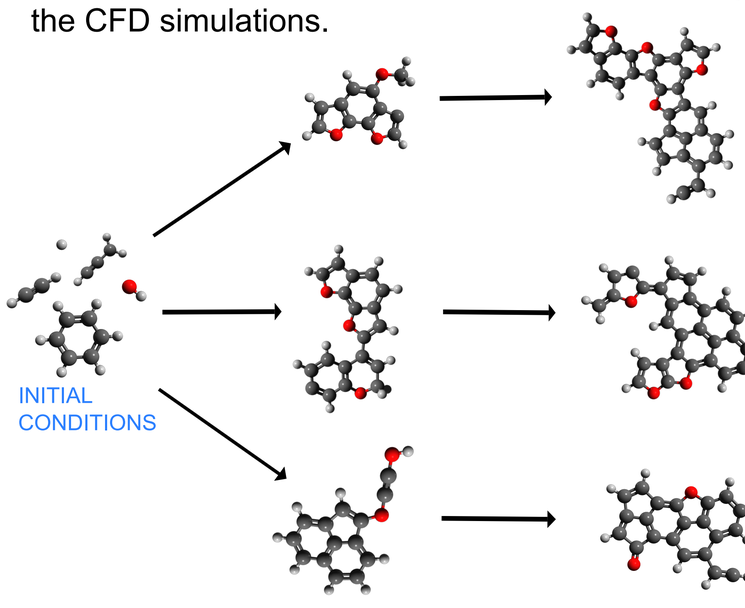

Fig. 1: Examples of trajectories identified by the SNapS2 code depicting the molecular growth of various PAHs, including oxy-PAHs. Oxygen atoms are in red, hydrogen atoms in white and carbon atoms in gray. Each SNapS2 trajectory selects reactions based on probabilities of reacting, and describes the particles growth history.

Experimental data:

Flame-sampling molecular-beam mass spectrometry (VUV-MBMS) and aerosol mass spectrometry (VUV-AMS) [*Johansson et al., PCI, 2017*].

System:

Atmospheric-pressure ethylene/oxygen/argon counterflow diffusion flame. The fuel side is composed of 0.23 slm C_2H_4 and 1.10 slm Ar; the oxidizer side supplied a mixture of 0.25 slm O_2 and 1.20 slm Ar.

PRELIMINARY RESULTS

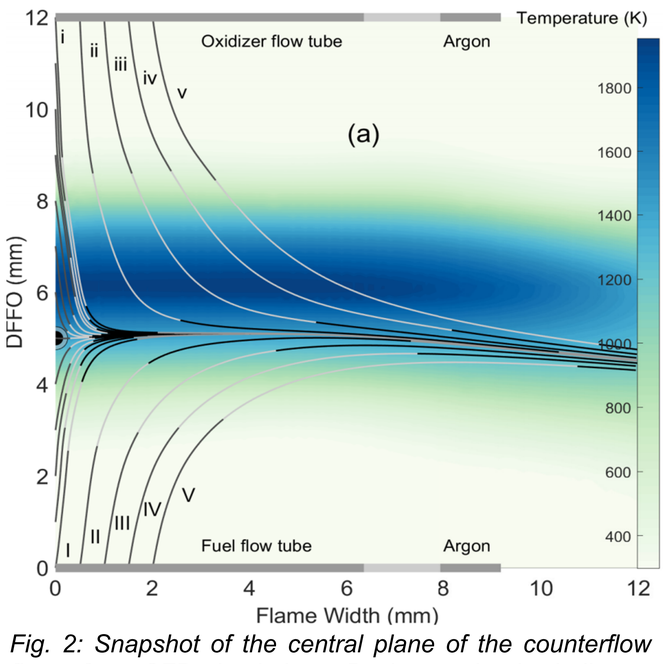

Fig. 2: Snapshot of the central plane of the counterflow flame from CFD simulations. Background color indicates temperature and lines represent flow streamlines.

Figure 2 shows a snapshot of the central plane of the CFD simulation results for the counterflow flame. The flame, located on the oxidizer side, is stabilized by the fuel diffusion across the stagnation plane, and has a maximum temperature of 1900K at 6.0 mm from the fuel side. Species profiles in Fig. 3 for streamline I and i, show how the evolutions of major species change along two different streamlines, highlighting the variations of gas-phase species between fuel and oxidizer side.

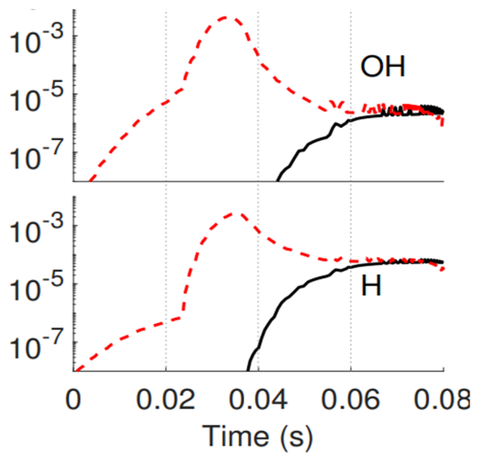

Fig.3: OH and H for streamline (I) and (i)

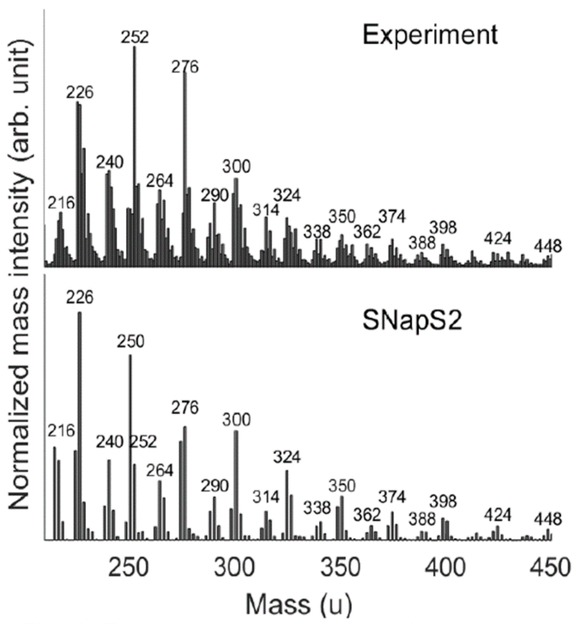

Fig. 4: Experimental and computed mass spectra at distance 5.0 mm from the fuel outlet.

Mass spectra produced by the SNapS2 code agree well with experimental data, obtained using VUV-AMS. The major peaks and their relative intensities are well-captured.

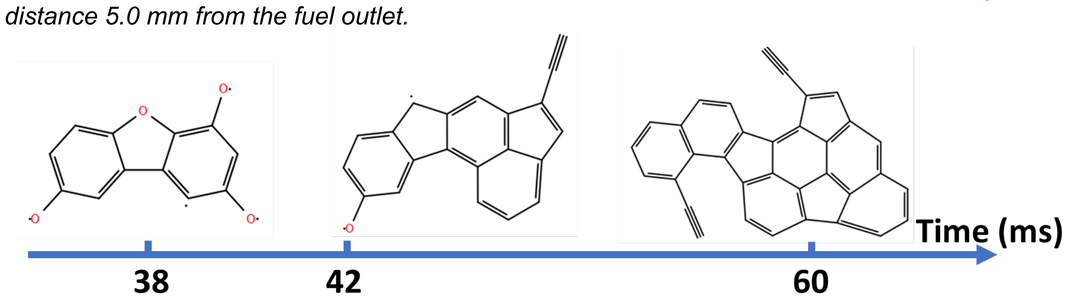

Fig. 5: Examples of molecular structures formed along streamline (i) at different times

Figure 5 shows examples of molecular structures formed along oxidizer-side streamline (i) at different times. At early stage, a significant number of oxygenated species are formed, with the presence of some furan-type structure. Later, the amount of oxygenated species decreases, and eventually hydrocarbons are mainly formed via HACA mechanism [*Frenklach et. al., PCI, 2005*].

IMPACT & CONCLUSIONS

This work highlights the formation of oxy-PAHs in a counterflow flame of pure hydrocarbons, emphasizing the need for a new chemistry of oxidation of PAHs that is currently not included in kinetic mechanisms. Further work will focus on reaction mechanisms for the interactions of PAHs and oxygen, especially furan-type compounds. The need for a predictive model that can reproduce the distribution and characteristics of compounds of incomplete combustion is of great importance. Indeed, oxygenated compounds can have detrimental effects on human health, air quality and climate. Indeed, furans are toxic and pose a serious threat to human health. Being able to predict their formation is therefore of great importance.

ACKNOWLEDGMENTS

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