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A kinetic modeling study of soot formation in cyclic C6 hydrocarbon flames

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Abstract

Soot formation is studied in premixed laminar flames of cyclic C6 hydrocarbons using a general and detailed kinetic model of gas phase combustion chemistry of several fuels coupled with a discrete sectional soot kinetic mechanism. Benzene and cyclohexane premixed flames in the same fuel-rich and temperature conditions are investigated in relation to the different pathways leading to soot. Comparisons between model predictions and experimental data permit us to understand the data more in detail and help to refine and validate the soot model.

Introduction

The formation of polycyclic aromatic hydrocarbons and fine particulate matter in combustion processes is a topic of continued research interest and critical gaps in the fundamental understanding of soot formation remain [1, 2]. These gaps include the role of the fuel chemical structure on soot formation. Aromatics and cycloalkanes play an important role in practical fuel chemistry due to their relevant presence in liquid transportation fuels [3]. Therefore the study of their combustion kinetics results very important especially at high temperatures, similar to engine conditions.

Because of the subtle differences in the fuel structures between cyclic C6 hydrocarbons, different pathways to aromatics and hence different rates to aromatic growth are expected. The fuel structure difference can impact the nucleation rate of soot and its subsequent mass and size growth, and such effect remains mostly un-explored for premixed flames.

In the last years, benzene and cyclohexane atmospheric, premixed and laminar flames were studied experimentally on a commercial water-cooled sintered bronze burner in order to understand the influence of the peak temperature of the flame [4,5], the influence of stoichiometry and fuel structure [6] on benzene and soot formation.

Moreover, recent data on soot growth in premixed C6 hydrocarbons flames in Burner Stabilized Stagnation (BSS) conditions [7] came out with details on the evolution of the detailed soot particle size distribution function (PSDF). The aim of this work is to use a gas phase kinetic model coupled with a soot mechanism to investigate these experimental data and to validate the soot model.

Kinetic Model and Numerical Method

Detailed gas-phase kinetic model [8] adopted here consists of about 200 species and 6300 reactions. It describes the high-temperature pyrolysis



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and oxidation of a wide range of hydrocarbons (<http://creckmodeling.chem.polimi.it/>). This mechanism was developed with a modular and hierarchical approach and it has been refined and validated over a wide range of conditions for the pyrolysis and oxidation of benzene [9] and for acetylene pyrolysis at high temperatures [10].

All numerical simulations were performed using OpenSMOKE code [11] for premixed flames and the code used for the pseudo one-dimensional formulation of counterflow reacting jets was adapted to the BSS flame configuration. The soot kinetic model is based on a discrete sectional method with an extensive use of lumping rules. Analogy and similarity rules with gas phase kinetics are used to extend soot mechanism up to the formation of species with more than 107 carbon atoms. The lumped approach, extensively applied in the kinetic modeling of large hydrocarbon species, becomes a need in treating chemical reacting systems of these dimensions.

The soot kinetic model is constituted by 20 classes of pseudo-species with increasing molecular mass. Each class is represented by a combination of lumped pseudo-species (called BINs), each with an assigned number of hydrogen and carbon atoms. Large PAHs, from 20 carbon atoms, constitute the classes BIN1-BIN4 and the first soot particles are considered formed by 320 carbons, that is BIN5. The particles are considered spherical, with diameters of up to ~60 nm.

Different H/C ratios for particles of the same class have been considered in order to describe the dehydrogenation reactions, the aging of the soot particles and the experimental evidences of the different degree of methylation of the pericondensed aromatic species. The same classes are considered for radical species. The estimation of the thermodynamic properties of the pseudo-species BINs was performed using the group additivity method of Benson.

The reaction mechanism was and is still largely developed by using analogy and similarity rules with the gas phase kinetics. The reference kinetic parameters of the different reaction classes involved in the soot kinetic mechanism are thus derived from the analogous reactions involved in the gas phase kinetics. The reactions were defined using an automatic generator, in which the kinetic rules are defined.

The processes of soot formation include nucleation, surface growth involving gas-surface reactions and PAH condensation, particle-particle coagulation with kinetic parameters appropriate for these processes. Oxidation by the O, OH and HO₂ radicals and molecular O₂ was considered, as well as H-abstraction, de-methylation and dehydrogenation reactions.

Results and discussion

The soot concentration was measured in laminar premixed benzene and cyclohexane flames, whose stoichiometric and operating conditions are reported in the Table 1. These flames have fixed carbon-to- oxygen ratio



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of 0.77 and maximum flame temperature of ~1730 K, in order to isolate these parameters from the fuel structure effect.

Fuel	ϕ	xFuel	xO ₂	xN ₂	C/O	v [cm/s]	Tmax [K]	P [atm]
Cyclohexane [6]	2.3	0.124	0.482	0.394	0.77		1722	1
Benzene [4]	1.9	0.049	0.19	0.761	0.77	4	1742	1
Benzene [5]	1.98	0.057	0.216	0.727	~0.8	3	1720	1

Table 1. Summary of the laminar premixed flame conditions.

Comparisons between experimental data and model predictions of benzene and cyclohexane flame structures are shown in the Figure 1. The model predicts fairly well the reactivity of the two flames.

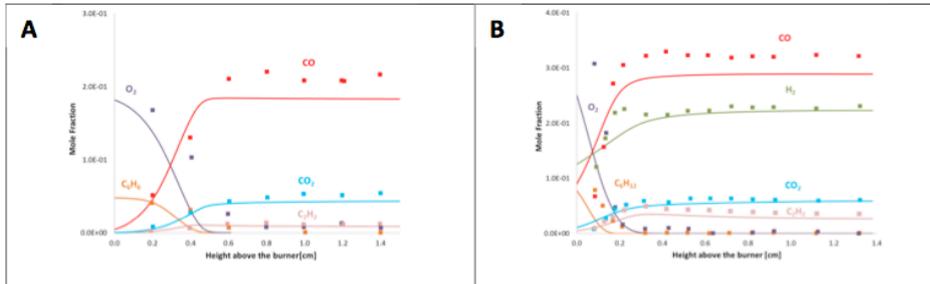


Figure 1. Benzene [4] (panel A) and cyclohexane [6] (panel B) flame structures. Experimental data: symbols. Model predictions: solid lines.

In panel A of Figure 2 is reported the comparison between the measured and predicted benzene concentration in the cyclohexane flame as key precursor to soot formation. The peak of benzene is well predicted by the model and it is mainly formed by the dehydrogenation of cyclohexadiene. In panel B of Figure 2 is shown the predicted and measured soot concentration in the three studied flames. The model predicts reasonably the soot formed in the cyclohexane flame, with a soot inception that starts at 0.4 cm and a plateau at higher heights above the burner. Local temperature is the dominant parameter which governs the soot chemistry and because of the difficulties in its measurement there are great experimental uncertainties on the temperature profile. In the benzene flames, the soot is underpredicted by the model but the experimental trend of soot growth in dependence of the fuel is fairly caught. Sooting tendency of aromatics is higher than that of cycloalkanes. The larger soot formation in cyclohexane flame is due to the higher fuel concentration.

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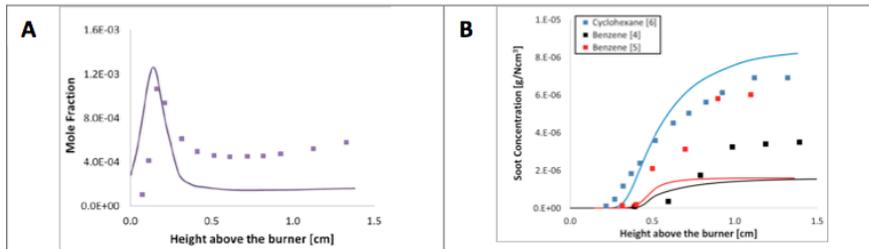


Figure 2. Panel A: benzene mole fraction in the cyclohexane flame [6]; Panel B: soot concentration in all the three flames [4-6]. Experimental data: symbols. Model predictions: solid lines.

Recently, similar benzene and cyclohexane flames are examined experimentally by Camacho et al. [7] using the BSS flame approach coupled with mobility sizing, described in detail elsewhere [12,13]. This method is employed to investigate the evolution of PSDFs in nascent soot from particle nucleation to mass growth of these C6 hydrocarbon flames. The studied flames have fixed carbon-to-oxygen ratio of 0.69 and maximum flame temperature of 1800 K, as reported in Table 2.

Fuel	ϕ	xFuel	xO ₂	xAr	C/O	v ^a [cm/s]	Tmax [K]	P [atm]
Cyclohexane [7]	2.07	0.0748	0.325	0.6002	0.69	4.87	~1800	1
Benzene [7]	1.72	0.0748	0.325	0.6002	0.69	3.41	~1800	1

^a STP cold gas velocity

Table 2. Summary of the premixed BSS flame conditions.

Panel A of Figure 3 shows the comparisons between the experimental and predicted soot volume fraction for BSS benzene and cyclohexane flames at different burner-stagnation plate distances (separation distance, H_p). In these conditions, the soot formed in the benzene flame is more than that formed in the cyclohexane flame and the model well predict this behavior and also each soot volume fraction.

In Panel B of Figure 3 is reported an example of measured and modeled PSDF of benzene flame in terms of surface area at $H_p = 0.8$ cm. Experimentally, it is observed not only a fastest onset of soot nucleation in flames of cyclic hydrocarbon fuels in respect to linear C6 hydrocarbons but also a faster disappearance of nucleation-size particles [7]. In this case, the model is not able to predict the disappearance of the soot nucleation and the agglomeration mode is related to small particles than the observed ones. This could be due to the missing agglomeration reactions that mostly count for these parent fuels.

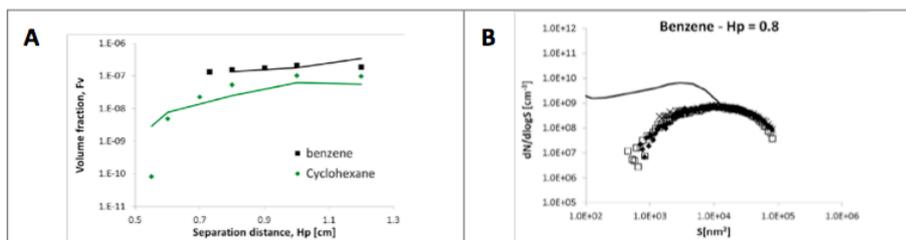


Figure 3. Panel A: soot volume fraction at different separation distances H_p in benzene and cyclohexane BSS flames [7]; Panel B: PSDF in terms of surface area of benzene flame at $H_p = 0.8$ cm [7]. Experimental data: symbols. Model predictions: solid lines.

Conclusions

In this work, benzene and cyclohexane premixed flames and BSS flames in similar fuel-rich and temperature conditions are numerically investigated in relation to the different pathways leading to soot. The

model is able to predict fairly well the available experimental data on soot concentration and volume fraction, but it has to be improved in order to reproduce the observed behavior of nascent soot from particle nucleation to mass growth in C6 hydrocarbon flames.

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