

# DETAILED KINETIC MODELING OF SOOT FORMATION AT LIGHTLY SOOTING CONDITIONS

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## Abstract

Soot particles formed in combustion processes are well-known for their negative effects, but their formation is still elusive and challenging. In particular, the main chemical and physical pathways are not fully understood. It is important to characterize soot not only in terms of mass yield but also to accurately characterize number density and particle size distribution (PSDF). The distribution of soot particles is essential to understand the soot evolution in a flame. The aim of this work is to revise and validate a detailed kinetic mechanism based on a discrete sectional approach for soot, with the aim to compare the model predictions with the measurement from Gu et al. (2016) in burner-stabilized stagnation (BSS) configuration. The lightly sooting condition flames ( $\phi = 1.8$ , 60% Ar, 1 atm) with different maximum temperatures are simulated using a pseudo-one-dimensional stagnation model. The predicted PSDF is in reasonable agreement with experimental results, but the model only partially reproduces the distinct separation between nucleation and coagulation modes observed experimentally at low-temperature (flame K3). The model predictions slightly underestimate the particle size at K3 flames, leading to the underprediction of soot volume fraction and number density. The predicted PSDF of high-temperature flames (K6) reproduces the unimodal distribution of nucleation tails observed experimentally. The flux analysis of benzene at the maximum temperature shows that the lower formation of soot particles could be a result of the thermodynamically reversibility to form gas-phase species at high temperature ( $>1750$  K). The predicted trends of soot number density and volume fraction of all flames are quite satisfactory. However, this study shows that further attention to the formation of PAHs and their condensation on soot particles is required.

## Introduction

Soot is a well-known pollutant for its negative effects on the environment, human health and the combustion efficiency. In particular to human health, soot particles are particulate matters that suspend in the atmosphere where the inhalable ultrafine particles can penetrate into lungs and bloodstream. These negative effects explain the efforts dedicated to the study of soot formation, particularly to understand the

not only the total amount of soot formation but also the evolution of the particle size distribution function. In fact, a more complete understanding of soot formation mechanism provides the opportunity to minimize its formation and emission.

The stack of polycyclic aromatic hydrocarbons (PAH) is widely accepted as the precursor to particle nucleation. The morphology of soot particles is observed experimentally to be strongly dependent on temperature, residence time and fuel characteristics [1], [2]. To better understand the soot evolution, the soot kinetic mechanism should be able to describe the different chemical and physical phenomena which affect soot formation and consumption.

The aim of this work is to validate the soot kinetic mechanism with the experiment study from Gu et al. (2016) [3] at the lightly sooting conditions of laminar premixed ethylene-oxygen-argon burner-stabilized stagnation (BSS) flames ( $\phi=1.8$ ). The K3 and K6 flames have the maximum temperature at 1826 and 1941 K, respectively. They are chosen to show the effect of temperature, whereas the measurements at different burner-to-stagnation separations represent the effect of different residence times.

### **Model Description and Numerical Simulations**

The soot mechanism is based on a discrete sectional approach and is coupled to the gas-phase kinetic mechanism to model the evolution from gas-phase species to solid particles. The model includes the discretization in mass size spectrum into 25 sections that are considered as lumped-pseudo species called “BINS”. Each BIN is further subdivided in sub-sections, labelled “A”, “B” and “C”, which represent different hydrogenation levels. The soot mechanism used in this work is the developed based the previous POLIMI soot mechanism proposed by [4] with the differences number of BINs and coagulation efficiency. The coagulation efficiency includes the dependency on temperature and particle size. The coagulation rate used in present work is  $1.6 \times 10^{12} T^{0.5} nC^{1/6} \text{ mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ , which includes the adoption of coagulation frequency adjustment factor based on a number of carbon atoms,  $nC$ , from [5]. The complete kinetic mechanism consists of ~350 species and ~25,000 reactions.

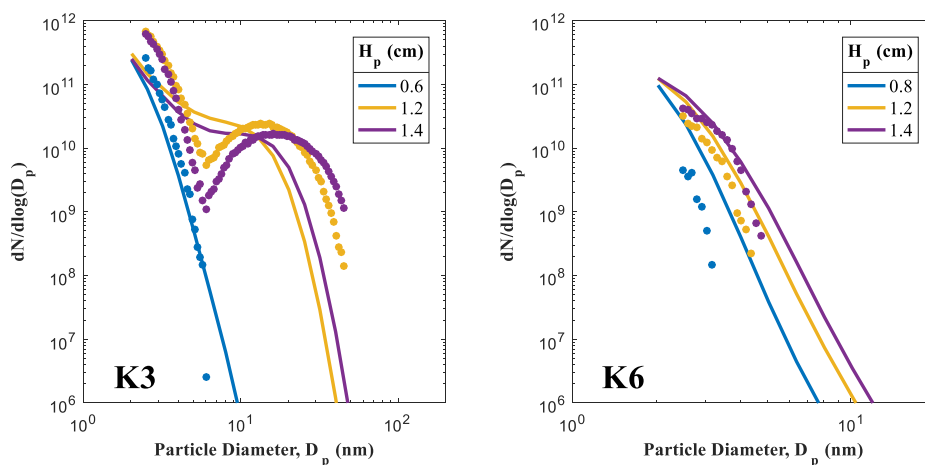
The BSS flames configuration, thanks to the well-defined boundary conditions, allows the pseudo-one-dimensional stagnation flow model to be performed. The numerical simulations were carried out with the OpenSMOKE code [6]. The probe effects of soot sampling in BSS flames were corrected by the spatial shift at the upstream of the plate as suggested by [7].

### **Results and Discussions**

Initially, the numerical simulations were performed with the pseudo-one-dimensional stagnation flow model using the measured temperatures at the burner surface and the stagnation plate. The model predictions were found to underestimate the maximum flame temperature. Therefore, the temperature profile is imposed to the simulation, and thus, the energy balance has not been solved. The

underestimation of maximum flame temperature is due to the elementary gas-phase kinetic scheme in which the relative reactivity of pyrolysis path is favoured over the oxidative path.

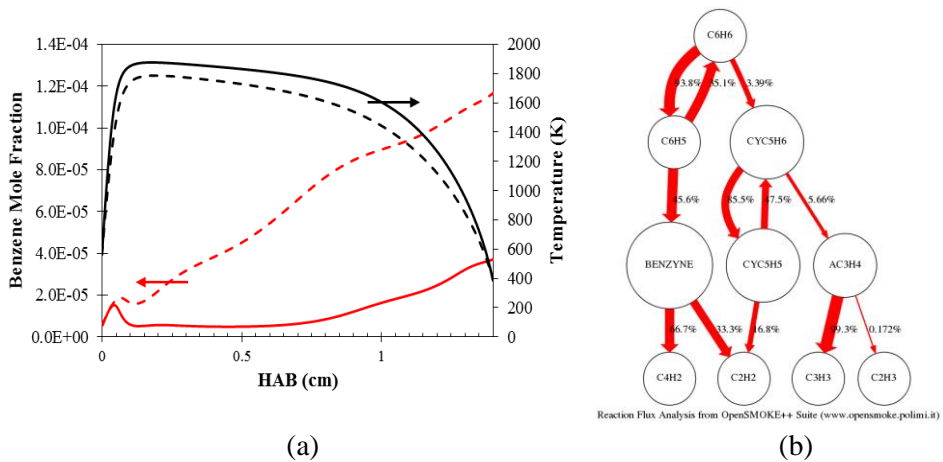
The comparison of particle size distribution function (PSDF) at each burner-to-stagnation separation distance ( $H_p$ ) between model predictions and the measurements is shown in Figure 1. The computed PSDF profiles show reasonable qualitative agreement with the experimental data. The measured PSDF of K3 flames the incipient soot region ( $H_p = 0.6$  cm) shows the unimodal distribution, in which is well predicted by the model. At long residence times ( $H_p = 1.2$  and 1.4 cm), the experiment show a clear bimodality in the PSDFs, which indicate the distinctive segregation between nucleation and coagulation modes. This behaviour is only partially captured by the model. In quantitative terms, the model results in general under-predict the measured particle size. At high-temperature conditions (flame K6), the observed PSDFs show only the unimodal distribution in all burner-to-stagnation separation distances. The model satisfactorily reproduces this behaviour, although it slightly over-predicts soot at the smallest separation distance ( $H_p = 0.8$  cm). The unimodal distribution at high temperature results from the PAH formation which is thermodynamically and kinetically controlled.



**Figure 1.** Comparison between computed (solid lines) and measured (symbols) PSDFs at different burner-to-stagnation surface separation distance. Different colors represent PSDFs at each separation distance (cm).

Figure 2a shows computed benzene and temperature profiles along the height above burner (HAB). The decrease of benzene mole fraction, starting at  $\sim 1750$  K, can be observed in both flames in the flame region. The temperature drops at the post-flame region, therefore, the benzene profiles increase again. The flux analysis of benzene at the maximum temperature of  $H_p = 1.4$  cm of K6 flame is shown in

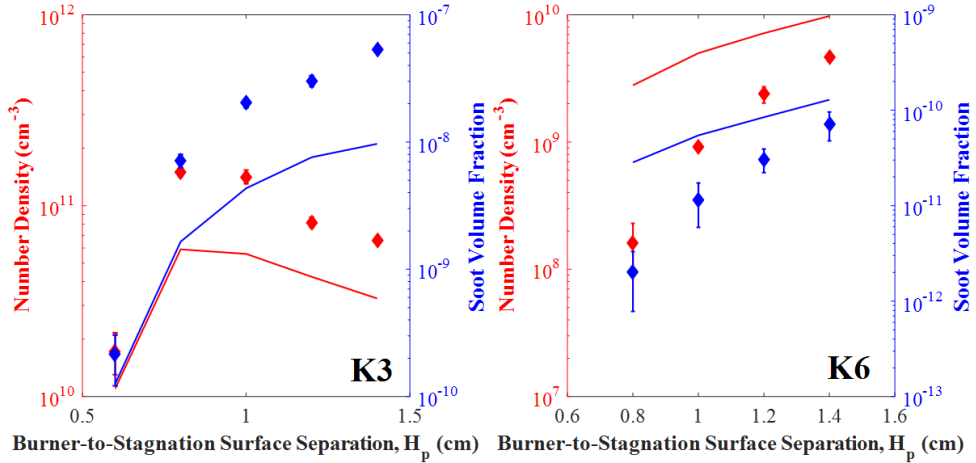
Figure 2b. It shows the thermodynamically reversible pathways of benzene to gas-phase species occurs mainly via phenyl radicals. The depletion of benzene to gas-phase species is important at high temperatures because it can compete with the molecular weight growth reactions that subsequently form soot. As a result, the soot formation at high temperature (K6) has less mass yield and smaller particle size comparing to the lower temperature flame (K3). This analysis of benzene profile and its destruction illustrate the importance of PAH in the soot formation model. These findings further highlight that further attention is needed for the prediction of PAH formation and its condensation to soot particles, especially as a function of temperature.



**Figure 2.** Left panel: comparison of temperature and computed benzene profiles between K3 and K6 flames at  $H_p = 1.4$  cm. Dashed lines indicate K3 flame and solid lines indicate K6 flame. Right panel: flux analysis of benzene at the maximum temperature of K6,  $H_p = 1.4$  cm.

Figure 3 show the comparisons of predicted and measured number density and soot volume fraction at each burner-to-stagnation separation distance. The predicted profiles of number density and soot volume fraction are quite qualitatively good. In particular, model predictions of K3 flames capture the experimentally observed peak in number density at  $H_p = 0.8$  cm followed by a slight decline. However, the model underestimates the measured soot number density and volume fraction profiles of K3 flames. The largest discrepancy of K3 flames is in the prediction of the soot volume fraction of mature soot at the largest separation distance ( $H_p = 1.4$  cm). This is the result of the underprediction of particle size that was shown for the PSDF profile. On the contrary, the number density and volume fraction profiles of K6 flames are found to be overestimated. The biggest differences between the model prediction and the measurements are at the smallest separation distance ( $H_p = 0.8$  cm), and is due to the overprediction of the number density of all particle

sizes. In general, the discrepancies between model prediction and the experiment are approximately within one order of magnitude in all conditions presented in this work.



**Figure 3.** Comparison between computed (solid lines) and measured (symbols) number density and soot volume fraction at a different burner-to-stagnation surface separation distance,  $H_p$ . Red color indicates soot number density, blue indicates soot volume fraction.

## Conclusions

The validation of a revised soot kinetic mechanism with the experimental studies of BSS premixed ethylene-oxygen-argon flames is presented. Several flames at lightly sooting conditions ( $\phi = 1.8$ ) at different maximum temperature are shown in this work. All numerical simulations are carried out with the pseudo-one-dimensional stagnation flow model with the imposed temperature. The soot results are taken at the spatial shift at the upstream of stagnation plane to the account the probe-induced effects that modify the local flow field in soot sampling.

The predicted PSDF of soot capture well the qualitative trends observed in the experimental data. At the low-temperature conditions (flame K3), the prediction of particle size is underestimated specifically for the mature soot particles. The PSDF shape predicted by the model can only partially capture the coagulation mode, while the experimental results indicate a more distinct segregation between nucleation and coagulation modes. On the contrary, the model predictions slightly over-predict particle size of young particles. The model predictions show the same unimodal distribution observed experimentally, which is the result of thermodynamical reversibility. The computed benzene profiles show the decline of benzene at high temperatures ( $>1750$  K) in which the flux analysis of benzene at the maximum temperature of K6 flame shows the depletion of benzene which leads

to C2-gas-phase species.

The model predictions of number density and soot volume fraction at each burner-to-stagnation separation provide reasonable agreement with the measurement, particular at the low-temperature flame (K3). The trend of number density profile of K3 flame is quite satisfactory as the model predictions can capture the rise and fall tendency in which demonstrates the effect of residence time on nucleation and coagulation of particles. However, the computed number density and soot volume in these conditions are slightly underpredicted.

At high-temperature flames (K6), the PSDFs exhibits only the nucleation mode. Consequently, the number density and soot volume tend to increase with residence time. The model prediction can capture this rising of particle formation quite nicely. However, the model marginally overpredicts the total amount of soot particles.

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