

A Simulation of Soot Formation Using Particle Dynamics with One Dimensional Nucleation Mode

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Abstract

Two soot formation models using particle dynamics with one-dimensional nucleation mode directly coupled with gas phase chemistry are tested on three ethylene and three methane laminar premixed flames. These models demonstrate strength in the prediction of concentration profiles of major combustion products and critical intermediates, and the characteristics of soot particles. These models extend the practicability of simulation beyond the prediction of soot volume fraction and estimate the mean particle diameter quite well especially for methane flames. In particular, our second model expands the range of fuels that can be simulated, and also correctly predicts the effects of C/O ratio on the soot formation process. The strength and weakness of these models are investigated and new features are identified for the development of next generation of soot models.

Introduction

Fuel combustion chemistry and soot formation process have been major areas of research of the combustion simulation community since a) soot particles are one of the major sources of air pollution; b) the radiation of soot particles is a major heat source in flames and fires. The combustion process from the ignition of fuel molecules to the formation of soot particles can be divided into three stages: gas phase chemistry, PAH formation and growth, and soot particle dynamics. There is an extensive literature on gas phase chemistry¹⁻⁵ and PAH formation and growth⁶⁻⁹. Recent reviews of the literature have been presented by Howard and coworkers¹⁰ and Frenklach¹¹. But there is still uncertainty in the mechanism in the formation of soot particle and particle growth and oxidation.

Polyynes, among recent models for soot precursors, are first proposed to soot particles by Homann and Wagner^{12,13} and recently Krestinin has developed the *Polyynne model*¹⁴ as a tool to study the means of soot formation. Other researchers believe that tar-like material or condensed hydrocarbon species (CHS) play an important role in the formation of soot particles¹⁵. D'Alessio and coworkers¹⁶ proposed that the soot particles are composed of small aromatic subunits with no more than two or three rings bridged by aliphatic bonds.

Frenklach and coworkers⁸ formulated the HACA (hydrogen abstraction carbon addition) model as the primary route for the PAH formation and growth. They extended this idea into the soot particle dynamics modeling with the development of a chemical lumping technique^{17,18}. The HACA model has been used to predict soot volume fraction for different C₂ fuels in PSR¹⁹ and laminar premixed flames²⁰. In order to simplify the mathematical formulation, pyrene was proposed as the basic soot building block and used as the only nucleation and condensation species and acetylene addition was employed as the backbone for the soot particle surface growth in these studies.

The recent development of the HACA model by Appel-Bockhorn-Frenklach²⁰ (ABF model) was successful in the prediction of soot volume fraction for several C₂ fuels but leaves room for improvement. For example, the soot volume fraction was predicted by treating α , the fraction of radical sites on surface that is available for acetylene addition, as a function of individual fuel type and initial conditions. Second, the existing HACA models do not predict well soot particle characteristics such as mean particle diameter.

The proposed refined soot models are based on the existing HACA models, using a similar chemical lumping technique to catch the chemical and physical properties of

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TABLE 1. Experimental Conditions of Six Atmospheric Flames (flow rate in mg/cm² s)

Flame ID	T _{max} (K)	Molar Composition			Flow Rate
		Fuel	O ₂	N ₂	
XSFC2H41.78	2110	14.0	18.0	68.0	7.96
XSFC2H41.88	1930	15.6	17.7	66.7	7.96
XSFC2H41.98	1910	17.0	17.4	65.6	6.17
XSFCH41.575	1960	53.5	46.5	0	5.69
XSFCH41.6	1940	54.5	45.5	0	5.65
XSFCH41.625	1850	55.6	44.4	0	5.61

soot formation and preserve the integrity of whole combustion chemistry.

Description of the model

We adopt the gas phase chemistry and PAH formation and growth model proposed by Appel et al. – the gas phase part of the ABF model – and the details of which are described elsewhere²⁰. However, we modify the particle dynamics routine of the ABF model and choose several aromatic compounds as the basic building blocks of soot particles, instead of a single species. There are a few good reasons for this modification. First, experimental evidence indicates the smallest subunits of soot particles are mainly two or three ring aromatics bridged by aliphatic bonds¹⁶. Second, the investigation of premixed methane flames done by Senkan and coworkers²¹ indicates that the use of pyrene alone cannot catch all the details of the effects of equivalence ratio ($\phi=2.2-2.6$) on the concentration profile of pyrene and soot concentration and size. We reduce the effects of this deficiency by using multiple condensation species as will be shown later. Third, cyclopenta-fused PAHs are abundant in combustion²² and based on the assumption that soot growth is substantially influenced by the kinetics of the soot precursors, we propose models including cyclopenta-fused PAHs to simulate soot particle dynamics with one dimensional nucleation mode.

The evolution of particle number density is governed by the general moment differential equations

$$\frac{dM_r}{dt} = R_r + G_r + W_r, \quad W_0 = 0, \quad G_1 = 0$$

where, R , G and W are the nucleation, coagulation and surface growth rate terms, respectively. M_r is the r th moment.

The *nucleation* is modeled here as the dimerization of certain PAH molecules. Since cyclopenta-fused PAHs are believed as very active precursors to more condensed PAHs and soot particles, in our first model to be discussed later we will use a one-dimensional cyclopenta-fused nucleation mode for the inception of the young soot particles – the lowest class in our chemical lumping technique. The *coagulation* is allowed for by the coalescence of two soot particles P_i and P_j to form a new

particle P_{i+j} where i and j are number of carbon atoms in the particle, a process assumed to occur at the collision frequency. The derivation of *surface growth* takes the same approach as the soot particle coagulation mode but with a collision frequency between a PAH molecule and a soot particle.

We use a universal α , fraction of radical sites that available for reaction, derived by linear regression on α 's fitted to match the experimental data of acetylene and ethylene flames¹⁹.

$$\alpha = \tanh\left(\frac{12.65 - 0.0056T}{\log \mu_1} - 1.38 + 0.00068T\right)$$

where μ_1 is the first size moment of soot particle size distribution.

Flame Investigated

The experimental data for the six flames investigated in this study are those reported by Faeth and coworkers at one atmosphere with a spectrum of equivalence ratio for methane²³ ($\phi=2.3-2.5$) and ethylene²⁴ ($\phi=2.34-2.94$) fuels. The information of these flames is summarized in Table 1. For the simplicity to refer these flames in later discussion, each flame is assigned a primary key called *Flame ID* composed of the initials of the authors, the type of fuel, the pressure in atmosphere, and the decimal part of C/O ratio.

The ABF mechanism has already been tested with good confidence for C₂ fuels and we will extend the practicability of our modified models into C₁ fuels in this study. The equivalence ratio of the selected flames varied from 2.3 to 3.0 for the same fuel, so that the effects of equivalence ratio on the formation of soot particles in these premixed flames can be studied and compared with the experimental evidence.

In addition to matching soot particle characteristics such as volume fraction, mean particle diameter and number density, the simulation results are compared with the measured concentration profiles of major combustion products, the rate of fuel consumption and evolution of critical intermediates. Unfortunately, the information of the formation of the first aromatic species and the growth of PAHs were not reported by Faeth and coworkers, thus the computed PAH cannot be compared with measurements for these flames. But the gas phase chemistry of the ABF model we adopted has been tested^{5,8,19,20} in several earlier studies.

Results

The PAH species we picked for the nucleation and surface condensation modes include a range of one to four rings which are composed of molecules and radicals, regular PAH with 6-membered rings and cyclopenta-fused aromatics. Our simulation results show that inclusion of these aromatics as growth species greatly

reduces the problems caused by using pyrene as the sole soot building block. In particular, our model can be used to simulate C_1 as well as C_2 flames and predict the mean particle diameters.

Model I: Nucleation species: acenaphthylene; Surface condensation species: acenaphthylene, cyclopentadienyl radical, 2-ethynyl naphthalene, 2-ethynyl naphthalene, phenyl radical

We tested model I using three ethylene flames reported by Faeth and coworkers²⁴.

In Figure 1, the predictions for the molar fraction profiles of four major combustion products are presented, since it is important that the model is able to match the concentration of the major species before it is applied to minor species and soot. As we see in Figure 1, all major products for every ethylene flame examined are predicted well, especially the concentration profile of carbon dioxide. The prediction of other three major products, carbon monoxide, water vapor and hydrogen gas, is within 10% deviation.

In figure 2, the predictions for the mole fraction profiles of fuel and other C_1 and C_2 species, namely, CH_4 and C_2H_2 , are presented. Acetylene is the most critical unit for PAH and soot particle growth in the HACA mechanism and its importance cannot be underestimated. The concentration of CH_4 is predicted within 10% of experimental values except at the lower C/O ratio, namely, C/O=0.78. The prediction of C_2H_2 formation and consumption is improved as the C/O ratio increases and has a deviation of only 10-15%. The consumption of C_2H_4 is also well predicted within 15% of experimental data and, more interestingly, the model catches the trend of

concentration increase after the reaction zone. The overall ability of model I to predict the major combustion products and critical intermediates is obviously demonstrated.

We next examine the ability of model I to predict soot particle characteristics. In figure 3, the mean soot particle diameter and soot volume fraction are reported for three ethylene flames. The model predicts the soot volume fraction very well. But the model underestimates the mean soot particle diameter except for the post flame zone for two flames with lower C/O ratio. From the evolution curve of soot volume fraction, we find the model matches the soot mass well but underestimates the mean diameter significantly, especially in reaction zone. Thus we believe the model has a higher nucleation rate in the reaction zone but a lower condensation rate in post flame zone. And the slow condensation rate may be the most critical reason for the lower prediction of mean particle diameter.

Although model I has been successfully used to simulate soot particle formation in ethylene flames, especially for flames with lower C/O ratio, it yields soot volume fraction for three methane premixed flames that are higher by a factor of five. Thus we formulated another soot particle dynamics model with a one dimensional nucleation mode.

Model II: Nucleation species: 2-ethynyl naphthalene; Condensation species: 2-ethynyl naphthalene, phenyl radical, phenanthryl radical, pyrly radical

We tested model II using the three methane flames²³ and three ethylene flames²⁴ reported by Faeth and coworkers.

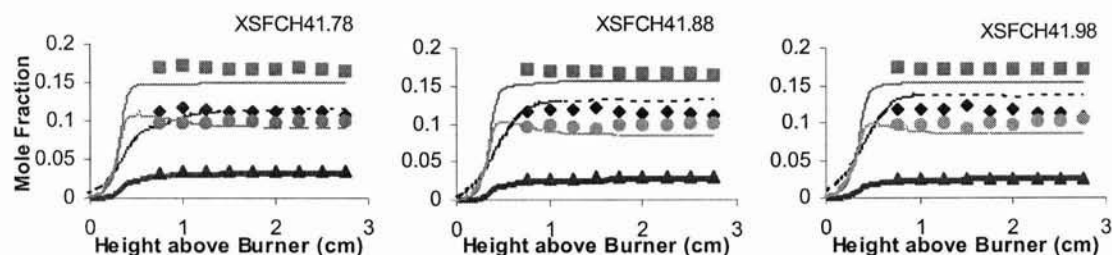


Figure 1. Concentration profiles for major combustion products of C_2H_4 flames using model I. Symbols, experimental data; Line, simulation results. CO, square, line; H_2 , diamond, dot line; H_2O , circle, dash line; CO_2 , triangle, heavy line

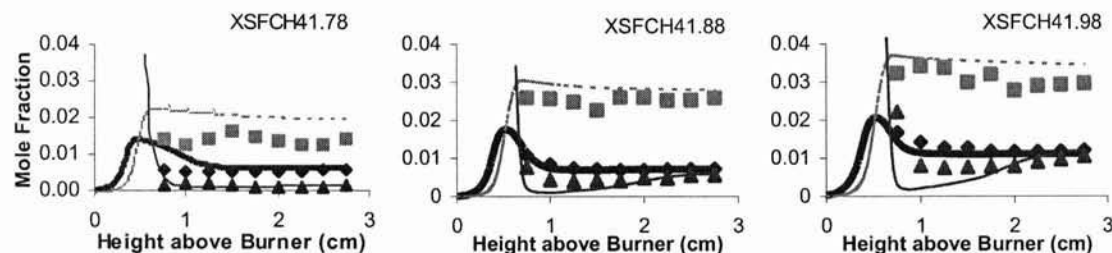


Figure 2. Concentration profiles for fuel and critical intermediates of three ethylene flames using model I. Symbols, experimental data; Line, simulation results. C_2H_2 , square, dot line; CH_4 , diamond, heavy line; C_2H_4 , triangle, line.

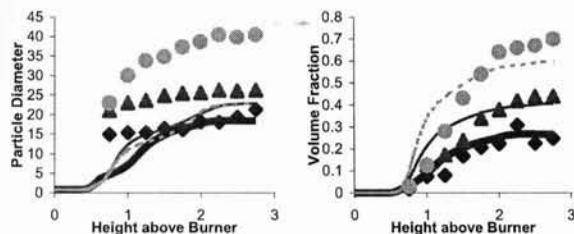


Figure 3. Mean particle diameter (in nm) and soot volume fraction (in ppm) of three ethylene flames using model I. Symbols, experimental data; Line, simulation results. XSFC2H41.98, circle, dot line; XSFC2H41.88, triangle, line; XSFC2H41.78, diamond, heavy line.

We will present our simulation results on three ethylene flames only for soot particle characteristics. There are no significant differences for the concentration profiles of major combustion products and critical intermediates between the predictions of model I and model II. But the prediction of soot particle characteristics is very different between the two models. In Figure 4, the prediction of soot volume fraction and mean particle diameter is reported. The soot volume fraction is underestimated for all three ethylene flames especially in the post flame zone by 40-55%. Only ethylene flame XSFC2H41.98 slightly overestimated the soot volume fraction in reaction zone and the other two ethylene flames simulations have almost perfect match. The model is able to predict the mean particle diameter in the post flame zone, especially for flame XSFC2H41.88, but greatly underestimated it in the reaction zone. In post flame zone, the simulation results of all three flames underestimated the mean particle diameters with the best case of 6% deviation for XSFC2H41.88 and worst case of 34% for XSFC2H41.78. There are 65-80% deviations in reaction zone between the experimental data and simulation results for mean particle diameters. Like model I, model II also has a too fast nucleation rate in reaction zone, but it is more complicated for the change in post flame zone. The nucleation rates are about same between simulation results and experimental data for flames XSFC2H41.98 and XSFC2H41.78 but slower for flame XSFC2H41.88. It is obvious that the slower condensation

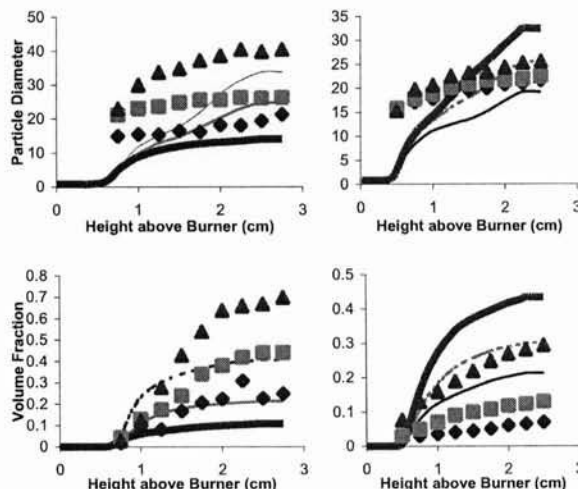


Figure 4. Mean particle diameter (in nm) and soot volume fraction (in ppm) of C_2H_4 and CH_4 flames using model II. Left: C_2H_4 Flames; Right: CH_4 Flames. Symbols, experimental data. XSFC2H41.98, triangle, line; XSFC2H41.88, square, XSFC2H41.78, diamond, Line, simulation results. Higher lines represent flames with larger C/O ratio.

rate should be blamed for the predictions of lower mean particle diameter in post flame zone.

We tested our second model on three methane flames not only on the concentration profiles of major combustion products and the characteristics of soot particles, but also on mole fraction profiles of critical intermediates.

In Figure 5, the prediction of the concentration profiles of major combustion products – carbon oxides, hydrogen and water vapor – is reported for three methane flames. The simulation results well predict the concentration profiles of carbon monoxide and carbon dioxide. The predicted concentration profiles of carbon dioxide are within 5% of the experimental data. The formation of carbon monoxides is underpredicted by 10-18%. The deviation is within the experimental uncertainty as reported by Faeth and coworker²³.

In Figure 6, the prediction for the molar fraction profiles of CH_4 fuel and two other C_2 species are reported. The predicted methane concentration profiles are only 2%

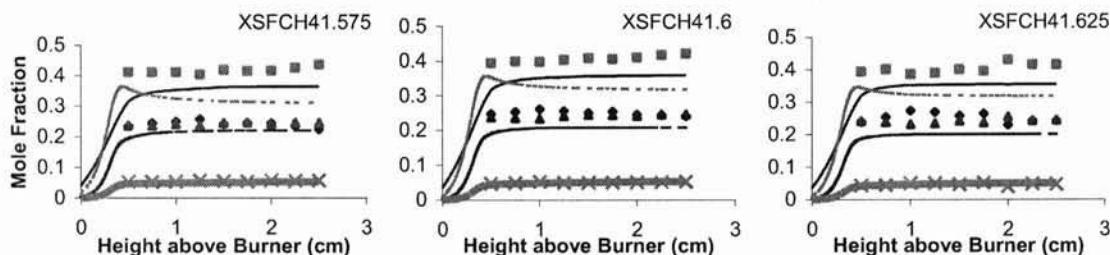


Figure 5. Concentration of major combustion products of three CH_4 flames using model II. Symbols, experimental data; Line, simulation results. H_2O , square, dot line; H_2 , diamond, line; CO , triangle, dash line; CO_2 , cross, heavy line.

higher than the experimental data for flames with lower C/O ratios. But the deviation becomes larger in the post flame zone. The predicted ethylene concentration is lower in the reaction zone and higher in the post flame zone. In the reaction zone, the deviation is 50-70%; in the post flame zone, the deviation is smallest for the flame with the lowest C/O ratio (deviation ~ 50%) and largest for that with highest C/O ratio (deviation ~ 150%). The concentrations of acetylene are overpredicted by 75% systematically in all three methane flames.

The predictions of soot particle characteristics for three methane flames are reported in Figure 4. Earlier we found in our simulation the nucleation rate is higher in the reaction zone but the condensation rate is lower in post flame zone for ethylene flames. For three methane flames, it is more difficult to identify a general trend of the predicted soot characteristics in comparison with the experimental results. One important difference between the experimental data of methane flames and those of ethylene flames is that the methane data set includes the measurements at the point of 0.5 cm above the burner. With the inclusion of these measurements, we find that our prediction of the soot formation process begins 0.1 cm later than the experimental data. After the formation process begins, the predicted soot formation rate accelerates and the soot volume fraction increases dramatically. The simulation results are higher than the measurements by a factor of three for the flame XSFCH41.575 and 135% and 45% higher than flames XSFCH41.6 and XSFCH41.625, respectively.

In the post flame zone, the predicted mean soot particle diameters are 26% and 14% higher than the experimental measurements for flames XSFCH41.6 and XSFCH41.625, respectively. The mean particle diameter is 11% lower than the experimental measurements for the flame XSFCH41.575 in the post flame zone. However, the predicted mean diameters are much lower than the experimental data in the reaction zone. At 0.75 cm above the burner, the model underestimated the mean diameter by 45-50% for all three methane flames and at 0.5 cm above the burner the deviations are as large as 80%.

We conclude the soot formation process begins about 0.1 cm later than the experimental measurements using

ABF model with coupled one-dimensional nucleation mode soot particle dynamics. The predicted soot formation rate is higher than the experimental measurements and leads to 45% - 200% overprediction for the soot volume fraction. The deviation in soot volume fraction increases as the C/O ratio decreases, with the worst case of 200% discrepancy for C/O equal to 0.575 and best one of 45% discrepancy for C/O ratio equal to 0.625. For the flame XSFCH41.6, the discrepancy is 135%. The predicted particle diameters for all three methane flames are about 50% lower than the experimental data in reaction zone. The deviations of mean particle diameters get smaller in the post flame zone and the discrepancies between the modeling and experiments for the mean particle diameters are 11-26%. Considering the profiles of soot volume fraction and mean particle diameters together, we found the nucleation rate is overpredicted in the reaction zone. In the post flame zone, the conclusion for each flame is different in the term of combined nucleation and surface condensation processes. For the flame XSFCH41.625, the nucleation rate is slower than experimental measurement and leads to 25% larger in mean diameters. For the flame XSFCH41.6, the modeling gives almost the same nucleation rate as the experimental measurement; however the faster surface condensation rate gives a mean particle diameter 14% larger. For the flame XSFCH41.575, the nucleation rate is faster than the experimental measurement and leads to a mean diameter 11% smaller.

Discussion

The current model has demonstrated the following advantages over a single aromatic species particle dynamics model. 1) The range of fuels that can be simulated is expanded. Our soot particle dynamics model with one-dimensional nucleation mode can be used not only to predict C₂ flames, but also the C₁ flames. 2) The effects of C/O ratio on the soot particle formation can be demonstrated. The difference of soot formation rate and soot characteristics can be distinguished under different sooting conditions. 3) The soot particle diameter is better fitted.

Recent developments in C₁ combustion chemistry

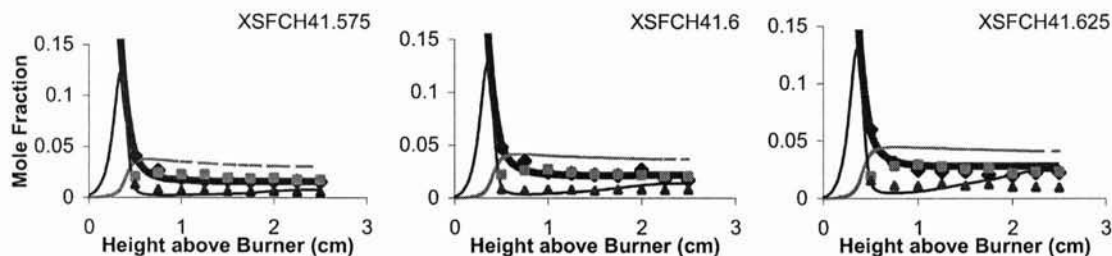


Figure 6. Concentration profiles for fuel and critical intermediates of three CH₄ flames using model II. Symbols, experimental data; Line, simulation results. C₂H₂, square, dash line; CH₄, diamond, heavy line; C₂H₄, triangle, line.

based on GRI mechanism^{25,26} have brought more and more reliable pathways for C₁ modeling. However the modeling of soot formation process with C₁ fuels gains little progress when we see a tremendous growth in literature of C₁ gas phase chemistry in experiments and simulations. Thus the ability to predict the soot formation process with C₁ fuels is a great achievement of this study.

But the weakness of models with one-dimensional nucleation mode is obvious too. In Figure 3 and 4, whether a physical property of the soot particle is over- or under-estimated is still not fully predictable. Thus a particle dynamics model with multi-dimensional nucleation mode is needed. The participation of multiple species in the nucleation process provides a better match of reaction rates under various flame conditions.

Another weakness of the current model is the use of collision frequency as the reaction rate for nucleation, coagulation and condensation processes. The use of collision frequency is based on the idea that a set of a few species can catch all the reactions between numerous aromatics in the soot formation process. Although this approach gives us a simple model and reduced CPU time, it takes a toll in the accuracy of simulation since the high rate will partially deplete those chosen species. Two deficiencies are: 1) the effects of some species on soot particle formation may be over emphasized; 2) the inaccurate concentration profile of a chosen intermediate can have complicating and cascading impacts on quite a few species.

Of course, the most accurate model will use realistic rate for every reaction in nucleation, coagulation, surface growth and condensation process. But this discrete approach is beyond the reach of current computing technology. Thus a chemical lumping technique is still a critical methodology for soot formation simulation. For the reaction of PAH or soot particles, $A_i + A_j = P$, a more accurate model using realistic reaction rates can be based on the technique of reaction classes. A possible approach will use a reaction rate as a function of the reactant size and chemical properties.

$$\frac{dP}{dt} = k_1(D_i, D_j)k_2(C_i, C_j)F x_i x_j$$

where x is concentration of reactants, k_1 is the size coefficient as a function of diameters of reactants, k_2 is the chemical property coefficient as a function of the permutation factors of species from different chemical categories, F is a fractal factor. This approach will be investigated in our future soot model development.

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