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A computational study of ethylene–air sooting flames: Effects of large polycyclic aromatic hydrocarbons

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ABSTRACT

An updated reduced gas-phase kinetic mechanism was developed and integrated with aerosol models to predict soot formation characteristics in ethylene nonpremixed and premixed flames. A primary objective is to investigate the sensitivity of the soot formation to various chemical pathways for large polycyclic aromatic hydrocarbons (PAH). The gas-phase chemical mechanism adopted the KAUST-Aramco PAH Mech 1.0, which utilized the AramcoMech 1.3 for gas-phase reactions validated for up to C2 fuels. In addition, PAH species up to coronene ($C_{24}H_{12}$ or A7) were included to describe the detailed formation pathways of soot precursors. In this study, the detailed chemical mechanism was reduced from 397 to 99 species using directed relation graph with expert knowledge (DRG-X) and sensitivity analysis. The method of moments with interpolative closure (MOMIC) was employed for the soot aerosol model. Counterflow nonpremixed flames at low strain rate sooting conditions were considered, for which the sensitivity of soot formation characteristics to different nucleation pathways were investigated. Premixed flame experiment data at different equivalence ratios were also used for validation. The findings show that higher PAH concentrations result in a higher soot nucleation rate, and that the total soot volume and average size of the particles are predicted in good agreement with experimental results. Subsequently, the effects of different pathways, with respect to pyrene- or coronene-based nucleation models, on the net soot formation rate were analyzed. It was found that the nucleation processes (i.e., soot inception) are sensitive to the choice of PAH precursors, and consideration of higher PAH species beyond pyrene is critical for accurate prediction of the overall soot formation.

1. Introduction

Soot formation is an important topic in combustion research, due to its negative impact on human health and the environment. Recently, the interests in soot models have expanded beyond the description of global soot properties, such as soot volume fraction and particle size distribution, to include detailed chemical and physical pathways that lead to the formation and destruction of soot particles in order to provide more accurate quantitative predictions of soot formation at a wide range of flame conditions [1]. Soot production is a complicated phenomenon involving many chemical and physical processes that are not yet understood completely. In the flame zone, the pyrolysis of hydrocarbons fuels leads to the formation of primarily smaller hydrocarbons, such as acetylene and propargyl. These species subsequently lead to the incipient benzene ring formation. The hydrogen-abstraction-C_2H_2-addition (HACA) mechanism, established by Frenklach and coworkers [2–4], plays an important role in the growth of polycyclic aromatic hydrocarbon (PAH) species prior to soot formation. It was also noted the odd-carbon number species, such as cyclopentadiene, indene are important to the formation of PAHs [5,6]. The growth of particle mass is a combined effects of chemical reactions with gaseous precursors simultaneously with PAH condensation [7,8]. Unlike surface growth that changes the total mass of soot particles, coagulation only changes the evolution of the soot particle size distribution [9]. In coalescent collision, two particles combine to form a single larger particle, while in agglomeration, two particles stick together to form a chain-like structure with the identity of individual particles maintained [10–12]. Simultaneously with these growth processes, oxidation of the aromatics also occurs as a critical destruction pathway [13]. One of the dominant mechanisms is proposed to be the free-edge oxidation of aromatics by oxygen molecules [14].

The soot mass and size distribution are the key quantities, and are characterized by the soot number density function (NDF), whose

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evolution is governed by the population balance equation [15]. Among several numerical approaches available, the Monte-Carlo [16], sectional [17], and moment methods are widely used. The method of moments is computationally efficient, by solving several lower-order moments of NDF instead of directly determining a large number of discrete NDF bins. The transport equations of the moment variables generate terms with higher or fractional order moments that need to be closed. While many variants have been proposed, the closure models may be classified into three approaches: the method of moments with interpolative closure (MOMIC) [18], the direct quadrature method of moments (DQMOM) [19] and the hybrid method of moments (HMOM) [20]. MOMIC is the most widely used approach with the equation for the highest moment closed by logarithmic polynomial interpolations and is adopted in the present study [21].

To describe the chemical processes of soot formation, a reliable gas phase kinetic mechanism is required. In this study, the KAUST-Aramco PAH Mech 1.0 was developed with PAH molecular growth up to coronene ($C_{24}H_{12}$), also referred to as A7 [22]. As compared with the earlier but widely used ABF PAH mechanism [10], the predictions of pyrene concentrations showed improved agreement with the experimental data. In most recent developments of detailed soot models [23–26], the primary particle is formed through the dimerization of pyrene ($C_{16}H_{10}$ or A4). As an attempt to enhance the soot nucleation rates, some of these studies made an unrealistic assumption that every collision leads to a successful creation of a soot nucleus. As a negative consequence, these models often under predict the gas-phase PAH species concentrations. This suggests that including only pyrene for nucleation may not be sufficient in describing the soot inception process. In fact, a recent study [27] reported that the larger PAH species have a stronger effect on the dimerization and soot inception, suggesting that higher PAH species need to be accounted for in comprehensive soot models.

To this end, the objective of the present study is to develop a comprehensive model to predict soot formation in ethylene–air non-premixed and premixed flames, thereby assessing the importance of the higher PAH species in the overall quantitative prediction of the soot formation. New comprehensive detailed and reduced reaction mechanisms were built from AramcoMech 1.3 [28] for gas-phase reactions for the fuels up to C2, which is coupled with a chemical pathway for PAH soot precursors up to A7. MOMIC was employed as a soot aerosol model. The reduced mechanism is first validated against the premixed and counterflow flames, for which measured PAH concentrations are available. The mechanism is an update from the previous KAUST Mech 2 (KM2) developed for lower hydrocarbon fuels [27]. An earlier KAUST Mech 1 (KM1) was to predict higher hydrocarbon fuels [29]. Based on the gas-phase mechanism, a soot nucleation model with 36 nucleation reactions was integrated following a similar procedure in a previous study of the KM2 [22]. Soot particle dynamics is solved using the method of moments for the sooting counterflow diffusion flames and premixed flames. In particular, two different nucleation models, one based on A4 and the other based on all higher PAHs up to A7, are considered and their relative impact on the overall soot prediction is evaluated and compared with the experimental data.

2. Model description

2.1. Gas-phase kinetic mechanism

The KAUST-Aramco PAH Mech 1.0 utilizes the comprehensively validated AramcoMech 1.3 C_0–C_2 chemistry developed by NUIG [28], and extends up to reactions involving benzene (C_6H_6 or A1). This mechanism contains accurate chemical kinetics for the combustion of saturated and unsaturated hydrocarbons, namely methane, ethane, ethylene, and acetylene, as well as oxygenated species, such as formaldehyde, methanol, acetaldehyde, and ethanol. On this base

$$r_{AB} \equiv \frac{\max_i |\nu_{Ai}\omega_i\delta_{Bi}|}{\max_i |\nu_{Ai}\omega_i|}$$

$$\delta_{Bi} = \begin{cases} 1, \text{if the } i^{\text{th}} \text{ reaction involves } B \\ 0, \text{otherwise} \end{cases}$$

ω_i: net reaction rate of the ith reaction
ν_{Ai}: stoichiometric coefficient of species A in the ith reaction.

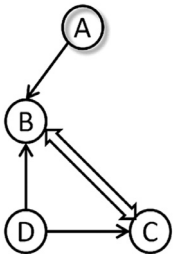

Fig. 1. Schematic of a directed relation graph. The importance of a species A with respect to B is described by a ratio of the importance of the reaction sensitivity.

mechanism, the formation of aromatics larger than benzene is accounted for by including the PAH growth pathways up to coronene for the capability to predict soot formation, which was previously implemented to KM1 [29] and KM2 [22]. The detailed KAUST-Aramco PAH Mech 1.0 has 397 species, including PAHs up to coronene (A7). The detailed mechanism was subsequently reduced to 99 species using the directed relation graph with expert knowledge (DRG-X) and DRG-aided sensitivity analysis (DRGASA) [30,31]. The resulting kinetic mechanism is a reduced version of the latest in a series of mechanisms developed at KAUST with improved accuracy in predicting the formation of PAHs, which are important precursors for the growth of soot [32]. The reduction effort is the initial step to enable efficient high fidelity simulations of multi-dimensional laminar and turbulent reacting flows for improved understanding of flow-soot interactions [33].

Figure 1 shows a schematic of the DRG method, which is based on the observation that many species are only weakly coupled during the combustion process, such that those species that do not significantly affect the reaction rates of the major species can be eliminated from the mechanism. DRG-X further allows for species-specific error control and was used in the preliminary reduction of the mechanism. The mechanism was reduced to 271 species from the detailed 397 species by assigning importance to PAH species. Additional reduction was accomplished using the sensitivity analysis of each species and control over the error of the target parameters including auto-ignition delay, extinction time in perfectly stirred reactors (PSR), and concentrations of important PAH species, resulting in 99 species. The reduction was performed for pressure of 0.1–10 atm, equivalence ratio of 0.5–5, initial temperature of 1000–1600 K for auto-ignition, and inlet temperature of 300 K for PSR, with ethylene as fuel and air as oxidizer. The comparison for ignition delay and the PSR extinction time are presented in Figs. 2 and 3, with good agreement between detailed and reduced mechanisms. Additional computational cost savings are achieved when additional reduction using quasi-steady state assumptions and dynamic stiffness removal are accomplished. To further validate the accuracy of the derived reduced mechanism, measured laminar flame speeds [34] are compared in Fig. 4, showing good agreement.

2.2. Heterogeneous soot model

In reference with the earlier work with heterogeneous mechanism mentioned in [27], a similar approach of surface reaction and soot dynamics approach is carried out to validate the reduced