

# **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 C<sub>2</sub> fuels. In addition, PAH species up to coronene (C<sub>24</sub>H<sub>12</sub> 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.

**Keywords:** soot model, laminar flames, method of moments, reduced mechanism, polycyclic aromatic hydrocarbon

## 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 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 in 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 nonpremixed 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 C<sub>2</sub>, which is coupled with a chemical pathways for PAH soot precursors up to A<sub>7</sub>. 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 A<sub>4</sub> and the other based on all higher PAHs up to A<sub>7</sub>, 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<sub>0</sub>-C<sub>2</sub> chemistry developed by NUIG [28], and extends up to reactions involving benzene (C<sub>6</sub>H<sub>6</sub> or A<sub>1</sub>). 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 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 Figure 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 mechanism. The following section summarizes the models for soot formation pathways.

### 2.2.1 Soot Nucleation

The PAH-based soot model consists of various pathways including soot nucleation, surface growth through HACA and PAH condensation, particle-particle coagulation, and oxidation reactions. Soot particle aggregation is not considered and particles are assumed to be spherical [11]. In the present approach, the inception of soot particles involves eight different PAH molecules, through homogeneous as well as heterogeneous nucleation reactions. Homogeneous nucleation involves self-addition of PAHs, while heterogeneous nucleation involves addition of two different PAHs. A total of 36 nucleation reaction steps are considered; these are physical processes and are assumed to be irreversible with zero activation energy [26], where one of the reaction in the surface mechanism part is shown as [35]



Each nucleation reaction rate is equal to the collision rate of the two precursors, given by [3],

$$R_{ci} = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \gamma \cdot C_E \cdot E_F \sqrt{\frac{4\pi K_b T}{\mu_{i,j}}} (D_i + D_j)^2 \cdot C_i \cdot C_j \cdot N_a^2 \quad (1)$$

where  $D_i$  &  $D_j$  is the collision diameter,  $C_i$  &  $C_j$  is the concentration, the subscripts  $i$  and  $j$  represents PAH species,  $C_E$  is the collision efficiency,  $\mu_{i,j}$  is the reduced mass,  $K_b$  is the Boltzmann constant,  $T$  is the flame temperature,  $N_a$  is the Avogadro constant, and  $E_F$  is the van der Waals factor. An important parameter is the correction factor,  $\gamma$ , which represents the probability of successful creation of a new soot nucleus when two PAHs collide. The correlation for the collision efficiency neglects the dependence on temperatures, and is determined by [35, 36]:

$$C_E = \frac{1}{1 + \exp \left[ -2 \left( \frac{D_{\min}^3}{m_{\min}} + \left( \frac{m_{\min}}{1100} \right)^6 - 5 \right) \right]} \quad (2)$$

where  $D_{\min}$  and  $m_{\min}$  are the collision diameter and mass of the smaller of the two colliding PAHs. The method of determining  $\gamma$  is explained by Wang et al. [27], in which the baseline pure ethylene flame was simulated by adjusting  $\gamma$ . It was shown that a satisfactory agreement between the simulated and experimentally observed maximum soot volume fraction was obtained with  $\gamma = 0.0052$ . For each mechanism under consideration, the  $\gamma$  value is adjusted only once and the same value is used for the entire parametric conditions.

### 2.2.2 Condensation & Surface Growth

Soot particle growth is described through surface reactions taking place on active sites. There are two types of surface sites involved in the model: (a) hydrogen sites where H atoms are bonded with carbon atoms, and (b) open sites indicating radical sites on dehydrogenated carbon atoms. These two types of sites are referred to as H(se) and open(se),

respectively. The overall site density, including both H(se) and open(se), was estimated to be  $3.82 \cdot 10^{-9} \text{ mol/cm}^2$  and the soot bulk density was taken to be  $1.8 \text{ g/cm}^3$ . The site density was used as a constant value, irrespective of the soot particle sizes. When a new soot nucleus is formed, its surface is covered by H(se) and open(se). The total number density is fixed while the number of H(se) sites is determined by the number of H atoms during PAHs inception [37]. No gas-phase species is generated in inception reactions. The number of open sites can then be calculated to balance the total number of surface sites.

### 2.2.3 Oxidation

Once soot particles are created in the flame zone, they start interacting with the surrounding gas mixture and with one another. If the oxidizers such as O, OH and O<sub>2</sub> are available in the gas mixture the soot particles are then subjected to oxidation. The most effective soot oxidizer in the flame zone is OH, given by [2],



In the case of soot formation (SF) flames, the flame is present in the oxidizer side, and the particles travel toward the stagnation plane. In this case, due to the absence of oxygen the oxidation rate is low and is only due to the presence of OH [38].

### 2.2.4 Soot Aerosol Model

Soot predictions in terms of its number density, diameter, and volume fraction are governed in detail by the particle size distribution function (PSDF), which are represented by the MOMIC in the present study. Given a particle-size distribution function  $n(j)$ , the  $r$ -th moment of the PSDF is defined as [18],

$$M_r = \int_0^{\infty} j^r \cdot n(j) \cdot dj \quad (3)$$

The particle-tracking module uses the particle class, i.e. the number of bulk species molecules in the particle core, as the measure of particle size. The zeroth moment of PSDF is the total number density of soot particles in a flame at a given position and time, while the first moment is the total mass density of soot particle. In principle, the knowledge of all the moments ( $r = 0, 1, 2, \dots, \infty$ ) is equivalent to the knowledge of the PSDF itself. In most practical applications, however, the properties of interest are determined by just the first few moments. The total mass of particle population is then calculated by [18],

$$m_{p,\Sigma} = \sum_{j=0}^{\infty} (j \cdot m_0) \cdot N_j \quad (4)$$

where  $N_j$  is the discrete PSDF of size class  $j$ . The average particle diameter of the spherical particles can be given by [35],

$$d_p = \frac{1}{N_{\Sigma}} \sum_{j=0}^{\infty} d_0 \cdot j^{1/3} \cdot N_j = d_0 \cdot \frac{M_{1/3}}{M_0} \quad (5)$$

Since the HACA growth pathways and PAH condensation are surface processes, the total particle surface area  $A$  is an important parameter in determining the rates of these processes. The total sphere-equivalent surface area of a particle population is given by [35],

$$A_{s,\Sigma} = \sum_{j=0}^{\infty} A_{s,0} \cdot j^{2/3} \cdot N_j = A_{s,0} \cdot M_{2/3} \quad (6)$$

A general definition of average diameters of the particle ensemble  $D_{pq}$  is then written as [39],

$$D_{pq} = \left[ \frac{\sum_{j=0}^{\infty} N(j) \cdot D(j)^p}{\sum_{j=0}^{\infty} N(j) \cdot D(j)^q} \right]^{\frac{1}{p-q}} \quad (7)$$

where  $D(j)$  is the particle diameter of size class  $j$ . A commonly used characteristic diameter is

$D_{63}$  defined as

$$D_{63} = \left[ \frac{\sum_{j=0}^{\infty} N(j) \cdot D(j)^6}{\sum_{j=0}^{\infty} N(j) \cdot D(j)^3} \right]^{1/3} = \left[ \frac{\sum_{j=0}^{\infty} N(j) \cdot \left( d_0 \cdot j^{1/3} \right)^6}{\sum_{j=0}^{\infty} N(j) \cdot \left( d_0 \cdot j^{1/3} \right)^3} \right] = d_0 \cdot \left( \frac{M_2}{M_1} \right)^{1/3} \quad (8)$$

where  $d_0$  is the minimum diameter of the bulk core, corresponding to a single carbon atom.

$D_{63}$  can be measured from experiments. All of the three moments implicitly represent the shape of the PSDF. To achieve closure of the moment equations, the fractional-order moments ( $M_{2/3}$ ) must be determined in terms of the integer-order moments that are solved.

In this study, therefore, the transport equations of 3 moments ( $r = 0, 1$  and  $2$ ) and surface4species were coupled with the gas-phase continuity, momentum, energy and species equations to obtain chemical and soot structures of counterflow nonpremixed flames through the OPPDIF module of CHEMKIN PRO [40].

## 2.3 Simulation Configuration

### 2.3.1 Nonpremixed flames

One-dimensional counterflow diffusion flame configuration is adopted for nonpremixed flame calculations. Following previous studies, depending on the level of dilution in the fuel and oxidizer streams, a soot formation (SF) flame can be established by placing the flame on the oxidizer side of a stagnation plane, such that the formed soot particles are advected toward the fuel stream without subsequent soot oxidation process. A soot formation/oxidation (SFO) flame occurs when the flame is located on the fuel side such that soot particles are transported toward the high temperature oxidizer side [41]. Due to oxidation, SFO flames demonstrate similar behavior to sooting premixed flames.

The present study investigates sooting behavior of ethylene nonpremixed flame in SF

configuration at the atmospheric pressure condition. Due to the availability of the experimental data, two different experimental measurements are used for comparison of PAH and soot predictions. For comparison of the gas-phase PAH species, the experimental results in Ref. [42] is used, with a 1.5 cm separation between the nozzles. The nozzle exit flow velocities for the fuel and oxidizer streams were set at 13.16 cm/s and 16.12 cm/s, respectively. The oxidizer stream was composed of 22% O<sub>2</sub> and 78% N<sub>2</sub>. The fuel stream was 75% C<sub>2</sub>H<sub>4</sub> and 25% N<sub>2</sub>. The prediction of soot volume is then compared with counterflow flame experimental data in Ref. [41] with a 1.42 cm nozzle separation and exit velocities of both fuel and oxidizer streams maintained at 19.5 cm/s. Fuel considered is pure ethylene and the oxidizer used was 76% N<sub>2</sub> and 24% O<sub>2</sub>. Computations are performed using the OPPDIF module of CHEMKIN PRO. For several representative cases, different grid parameters were tested to ensure grid convergence for all solutions reported in the following.

### 2.3.2 Premixed flames

A premixed flame calculation was carried out using the PREMIX code in CHEMKIN PRO for ethylene/O<sub>2</sub>/N<sub>2</sub> at atmospheric pressure and reactant mole fractions at C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 21.3/20.9/57.8 ( $\phi = 3.06$ ) [43]. To study the soot characteristics of the flame, the configurations of the flames considered were C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 14.08/18.05/67.87 ( $\phi = 2.34$ ), C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 15.60/17.73/66.67 ( $\phi = 2.64$ ) [44, 45]. These flames were generated using the McKenna burner and are covered with the nitrogen shield of gases to prevent secondary diffusion flame. These flames are also listed as target flames for the International Sooting Flame (ISF) [46].

## 3. Results and Discussion

To demonstrate the PAH species prediction using the detailed and reduced

mechanisms the simulation of flame setup is compared with the experiment [43]. Figure 5 shows the comparison of predicted PAH species profiles, A1, A2, A4 and A7. Although not shown, the profiles of the main combustion products, such as CO<sub>2</sub>, CO and H<sub>2</sub>O are predicted accurately.

In addition to the detailed and reduced mechanisms employed in the present study, calculations for PAH species using the KM2 mechanism are also shown for comparison. Both detailed and reduced KAUST-Aramco mechanisms show good agreement with each other, while some differences observed in comparison with the predictions by the KM2 mechanism. In particular, about an order of magnitude differences in the coronene mole fraction are observed. Unfortunately, no experimental data were available for A7 concentration, making the assessment of the fidelity of the two reaction mechanisms inconclusive. The spatial shift in the PAH profiles shown in Figure 5 is consistent with the findings in Ref. [47]; further investigation is needed to understand the exact cause.

A basic flame structure from the simulation of sooting flame configuration [41] is presented in Figure 6, where the temperature and axial gas velocity profile are presented. The stagnation plane is located around 0.5 cm, and the flame position is around 0.8 cm, where the maximum temperature is reached.

Next, detailed investigations are conducted to identify the contributions of various pathways to the overall soot mass growth rate. Figure 7 shows the predictions using the detailed (dotted line with symbols) and reduced (solid line) KAUST-Aramco mechanisms for the contributions of the nucleation, HACA surface growth, PAH condensation, respectively, to the net soot growth rate profiles. The net effect on the particle number density prediction is also shown. The overall qualitative behavior in terms of the peak location and the width of the profiles is found to be consistent between the two reaction mechanisms. For example, the

HACA surface growth rate reaches a maximum at a region near 0.72 cm, which coincides with the C<sub>2</sub>H<sub>2</sub> concentration peak at a distance of 0.65 cm combined with the temperature effect. In comparison, the surface growth rate due to PAH condensation occurs in a slightly wider region with a peak closer to the fuel side as expected. In contrast to the remarkably good agreement in the PAH concentration predictions by the detailed and reduced mechanisms (Figure 5), however, Figure 7 shows that there are noticeable differences in the predictions of the surface growth rate by all individual pathways. The nucleation surface reactions involve a total of eight PAH species, and additional gas-phase species, such as benzo(a)pyrene, benzo(e)pyrene, are under-predicted by the reduced mechanism, resulting in differences in the hydrogen open site and associated HACA growth paths. This reduction in particle growth rate subsequently leads to the same level of differences in the net prediction in the soot volume fraction, as will be discussed next.

The present reaction mechanism considered detailed nucleation pathways involving PAHs up to A7, while most previous detailed reaction mechanisms considered up to A4. To assess the significance of the additional pathways contributed by A5-A7, a contrived numerical experiment was conducted by truncating all gas-phase nucleation reactions including A5-A7. This case is referred to as “A4-only” reaction mechanism. As discussed in Section 2.2.1, soot nucleation rate parameters are determined following the same procedure, with a newly adjusted parameter  $\gamma$  with a baseline flame data.

Figure 8 shows the comparison of the soot volume fraction profiles predicted by the detailed, reduced, and A4-only mechanisms. The differences between the detailed and reduced mechanism results reflect the observation in Figure 8. Both results, however, show good agreement with the experimental measurements within a small margin of uncertainties. On the other hand, the A4-only mechanism yields a significantly under-predicted soot

volume fraction. The main difference is attributed primarily to the contributions from the PAH condensation, which is significantly enhanced in the presence of larger PAH molecules.

In Figure 9, the computed  $D_{63}$  from equation (8) is compared with the experiment. The agreement between the detailed and reduced mechanisms is good, while the prediction using the A4-only mechanism is significantly lower. This is attributed to a direct outcome of the lower soot volume prediction shown in Figure 8. Considering the complex morphology of soot particles, however, direct comparison of  $D_{63}$  with the experimental measurement must be interpreted carefully. It is also noted that the effect of the oxidation reactions to the soot growth process was found to be of less significance in the SF flame configuration under study. Future work will assess the accuracy of the model prediction in the SFO flames.

In Figure 10, the predictions of A1-A7 species mole fractions as function of the height of the burner (HAB) are presented. The reduced mechanism agrees well with the detailed mechanism, especially for the large PAH species, and both modeling results show good agreement with the experimental measurements.

As an alternative to assessing the soot model in an oxidizing flame environment, selected premixed flame configurations are considered for comparison. Figure 11 shows a comparison between predicted and measured soot volume fraction as a function of the height above the burner surface (HAB). The growth of soot formation is noted to begin at 2.5mm downstream of the burner, followed by a continuous rise due to surface and coalescence growth. As such, the present soot model (with heterogeneous nucleation) is considered to yield good agreement with the experimental data in comparison with the A4-only nucleation mechanism. Furthermore, experimental data measured using sampling [44] and laser extinction [45] techniques show different soot characteristics for the similar flame

configuration, suggesting significant uncertainties associated with experimental techniques, and thus the accuracy of the model prediction must be interpreted with caution.

The average diameter near the burner in Figure 12 shows a linear growth of PAH species initiates around 0.25cm from the burner surface, which is predominantly due to the growth of coronene, a major species, involved in soot nucleation up to 0.5cm away from the burner. The other PAH species start to form after this point to further increase the average diameter, as well as contribute to increase in particle number density. The differences in the simulated data is not surprising, considering that the experimental measurement using the TEM grid typically sets the upper limit as the soot particles impinging on the TEM grid. This is because of flattening of the soot particles on hitting the TEM grid. The diameter by the definition of  $D_{63}$  can also be calculated from the experimental data, assuming that the soot aggregate is spherical in shape [48]. Given the uncertainties associated with the definition and measurement errors for  $D_{63}$  quantity, the model based on the reduced mechanism yields reasonable predictions against the experimental data.

## 4. Conclusions

An updated detailed and reduced kinetic mechanism for soot formation in ethylene flames was developed and applied to selected nonpremixed and premixed sooting flame simulations. The mechanism was built based on the latest Aramco Mech 1.0 validated for C1-C2 fuels [28], augmented with kinetic pathways of PAH formation up to A7 [22]. A reduced mechanism was also developed using the DRG technique [30]. A method of moment with interpolative closure (MOMIC) [18] with three moment variables was used to predict soot formation, with an updated heterogeneous soot pathways following Ref. [27]. Due to the

limited availabilities in experimental data, different experimental configurations were used for comparison of various observables, such as PAH, soot volume, and soot diameter.

For both nonpremixed and premixed flames under consideration, predictions of PAH species were found to be in good agreement with experiment, at the level of agreement comparable to the predictions by the KM2 mechanism. The predictions of the soot volume fraction and average diameter also showed good agreement with experimental measurement available from various sources.

Subsequently, a computational experiment was conducted to assess the importance of higher PAH soot precursors on the soot formation by comparing with the simulations based on a truncated PAH mechanism only up to pyrene (A4). The results showed that the higher (A5-A7) PAH species are indeed important in quantitative prediction of the net soot formation. The A4-only mechanism yielded a significant under-prediction of the soot volume when compared with experimental measurements, suggesting that the consideration of higher PAH species as soot precursors is important in accurate soot prediction.

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## Figure Captions

Figure 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.

Figure 2. Ignition delay predictions using the detailed (line) and reduced (symbols) mechanism under different pressures and equivalence ratios.

Figure 3. Temperature profiles in PSRs for ethylene/air under different pressures and equivalence ratios using detailed (line) and reduced (symbols) mechanism.

Figure 4. Laminar flame speed versus equivalence ratio,  $P=1$  atm,  $T=298$  K; the results from the detailed and reduced mechanisms are compared with the experiment [34].

Figure 5. PAH mole fraction profiles in counterflow diffusion flame. Predictions using the detailed and reduced mechanisms are compared with experimental measurements [42].

Figure 6. Flame structure from numerical simulation of a counterflow diffusion flame.

Figure 7. Predictions of various pathways contributing to the soot particle growth.

Figure 8. Soot volume fraction profiles predicted by the detailed reduced A4-only mechanisms compared with the experimental data [41].

Figure 9. Average particle diameter profiles predicted by the detailed, reduced, A4-only mechanisms compared with the experimental data [41].

Figure 10. PAH species mole fraction profiles in premixed flames. Predictions using the detailed and reduced models are compared with experimental measurements [43].

Figure 11. Soot volume fractions predicted with the reduced mechanism for  $\phi=2.34$  (left) &  $\phi=2.64$  (right). Symbols are experiments [44, 45].

Figure 12. Average particle diameter for  $\phi=2.34$  (left) &  $\phi=2.64$  (right) predicted using the reduced mechanism compared with the experimental data [44].