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Soot formation with C₁ and C₂ fuels using a novel chemical mechanism for PAH growth

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Abstract

Recently, an improved chemical mechanism of PAH growth was developed and tested in soot computations for a laminar co-flow non-premixed ethylene-air diffusion flame. In the present work, the chemical mechanism was enhanced further to accommodate the PAH gas phase growth in methane, ethylene and ethane co-flow flames. The changes in the mechanism were tested on a methane/oxygen and two ethane/oxygen premixed flames to ensure no degradation in its application to C_2 fuels. The major soot precursors were predicted in a satisfactory manner. The robustness of the soot solution methodology was tested for different fuels by solving methane/air, ethane/air and ethylene/air co-flow laminar diffusion flames using a *single* solution algorithm for all three cases. The peak soot volume fractions, which varied by two orders of magnitude between fuels, were predicted within a factor of two for all flames. The computations were also able to reproduce the spatial distributions of soot and to explain the variation in soot formation pathways among the fuels. Despite a similarity in bulk properties of the flame, the soot particles in different flames exhibit significantly different growth modes. Ethylene/air flames tend to form soot earlier than methane/air flames and inception plays a bigger role in the latter.

1 Introduction.

Soot is a health, environmental, mechanical and aesthetical hazard and many efforts have been made in recent years to understand its behavior and to produce a reliable model for predictions of soot levels in combustion systems. Soot modelers face two main challenges – the first is to model correctly the PAH gas-phase chemistry that leads to the soot particle nucleation, and the second is to model the particle growth and oxidation in a manner that reflects the physical processes in the flame.

A common model of soot particle nucleation is the collision of two pyrene molecules in the free-molecular regime [1]. Many chemical mechanisms assume that the main path towards pyrene is the hydrogen-abstraction-carbon-addition (HACA) pathway [2]. In HACA, benzene grows to pyrene via acetylene addition. However, it has been shown that HACA based mechanisms do not provide a sufficient level of pyrene production [3,4]. Slavinskaya and Frank [5] suggested a reaction mechanism that incorporated additional pathways towards pyrene creation, which was updated later [3,4]. It was shown that use of this mechanism improved the prediction of the pyrene concentrations [4] and of the soot volume fractions [3] relative to previously tried chemical mechanisms. Since the publication of the previous work [5] additional information regarding elementary steps in the aromatic compound formation has been developed. Raj et al. [6] developed a kinetic Monte Carlo–aromatic site (KMC-ARS) model which describes continuous growth of PAHs to soot particles. Their detailed gas-phase PAH growth mechanism is based on the reaction rates available in the literature. New rate coefficients for the reactions involved in the cyclodehydrogenation process for the formation of 6-member rings on PAHs at low pressure (2.67 kPa) have been calculated in their work based on the density functional theory simulations. Narayanaswamy et al. [7] presented a consistent chemical mechanism to predict high temperature combustion of various substituted aromatic compounds. The reactions representing oxidation of the aromatic species are taken from the literature or are derived from those of the lower aromatics or the corresponding alkane species. Shukla and Koshi [8] examined experimentally collaboration of phenyl addition/cyclization (PAC), methyl addition/cyclization (MAC) and a hydrogen abstraction/acetylene addition (HACA) mechanisms by detecting the gas phase reaction products of pyrolysis of toluene with/without addition of benzene + acetylene. Their work demonstrates high efficiency of all mechanisms of PAH growth and their interdependencies. Individually, PAC was found to be dominant for endless ring

growth (it can continue growing indefinitely since it continuously generates new sites for the next aromatic ring), HACA for filling triple fusing site and MAC for expanding cyclotetra/pentafused into benzenoid structure, respectively.

In non-premixed flames, once the soot particle is inceptioned, it experiences the processes of aggregation, surface growth and later – oxidation. Soot particles are aggregates [9] of primary spherules and a fundamental model has to take this into account. One approach is to use the sectional method [10,11], in which the primary particles are divided into sections according to their mass [12-14], and aggregates are divided in a similar way according to a number of primary particles per aggregate [15-17].

Surface growth is believed to be dominated by two major processes [1]. The first is the condensation of PAH species on the particle. The second is the growth through HACA, where acetylene is the source of the carbon. The growth due to acetylene addition is a function of the chemical reaction rates in the HACA pathway and of the empirical parameter α , which reconciles the inaccuracies in treating sites on the soot surface as corresponding sites on gaseous PAH molecules. Dworkin et al. [3], Chernov et al. [18] and Eaves et al. [19] used constant values of α for ethylene (both non-premixed and partially premixed) and ethane co-flow flames and obtained good agreement with experiments. A constant value of α is also used in the present co-flow computations.

Most detailed soot models that have achieved quantitative accuracy have done so for a single fuel or family of fuels (e.g. C_2 fuels: ethylene, ethane and acetylene). This is because the character of soot precursor formation tends to change with different fuels, and accurate models usually include some tuning. A relatively small amount of studies have applied a single soot model to several different fuels. Blanquart and Pitsch [20] computed soot volume fractions using the method of moments for acetylene, ethylene, benzene and toluene in premixed flames,

counter-flow diffusion flames, and shock-tubes and obtained good agreements with experimental results. However, no PAH concentrations were reported. Blacha et al. [21] used the reduced version of Slavinskaya and Frank mechanism [5] and tested a PAH-soot combined sectional model that did not include representation of soot aggregates. They applied their model to several premixed flames (ethylene, propylene and toluene) and to co-flow ethylene flames (both diffusion and partially-premixed). The obtained results were in good agreement with the experimental data. However, it is not clear whether their model would cope well with a fuel change in the non-premixed and partially-premixed cases. They also do not report the PAH concentrations.

With the increasing usage of natural gas composed of light fuels, there is an unfulfilled need for a detailed soot model that would be applicable to them. The value of a detailed model goes beyond the obvious advantage of correctly modeling laminar flames; it is also a vital step toward the modeling of practical devices.

Accurately modeling soot growth for both C_1 and C_2 fuel is considered an important test of the model as significant differences exist in the flames. These differences include the makeup of the radical pool, the acetylene profiles, the pathways to PAH creation, and particle residence times. Therefore, a model tuned to one system would likely result in failure in another system. The present work attempts to overcome this problem and seeks to extend an ethylene flame soot model to methane and ethane by enhancing the soot precursor chemistry sub-model, while maintaining the integrity of the model as it applies to ethylene. It tests a modified version of the chemical mechanism (first presented by Slavinskaya and Frank [5], updated in later by Dworkin et al. [3], Slavinskaya et al. [4], and in the present work). Firstly, the modifications of the mechanism are verified for three premixed flames [22-24]. Secondly, the modified mechanism is coupled with a detailed sectional soot model and is tested on three different laminar co-flow

diffusion flames. The fuels tested are methane, ethylene and ethane. The Parallel CoFlame Code was used in all cases to solve the co-flow flames, and only the geometry and boundary conditions were altered to accommodate different datasets. The results are compared to the experimental data of Lee et al. [25] for the methane co-flow flame, Köylü et al. [26] for the ethylene co-flow flame and Mandatori and Gülder [27] for the ethane co-flow flame.

2 Problem formulation.

2.1 Burner and flame descriptions.

Three premixed flames were simulated to examine the influence of the changes in the gas-phase mechanism on the soot precursors concentrations. One was methane/oxygen flame and two were ethane/oxygen flames. For these flames no soot computations were made. The methane flame is modeled after the work of Aflé et al. [23]. A premixed laminar flat flames burner is used. The flame is a rich, premixed flame of CH_4/O_2 , at fuel to air ratio of $\phi = 2.4$. Cold gas flow velocity was 4 m/sec.

The ethane flames are modeled after the work of Melton et al. [22] and Castaldi and Senkaw [24]. A premixed laminar flat burner is used in both works. The flame is a rich, premixed flame of $\text{C}_2\text{H}_6/\text{O}_2/\text{Ar}$ at fuel to air ratio of $\phi = 2.6$. Melton et al. [22] burned flames at fuel to air ratios between $\phi = 2$ and $\phi = 2.6$, but for our verification purposes, only $\phi = 2.6$ was examined. Cold gas velocities were 6.19 m/s for Melton et al. [22] and 6.26 m/s for Castaldi and Senkaw [24].

Three co-flow laminar diffusion flames were simulated to examine the change in the gas-phase mechanism on the soot volume fractions. Methane, ethylene and ethane flames were used. The methane co-flow flame is modeled after the work of Lee et al. [25]. This work uses the Santoro [28] burner in which the fuel flows from a center tube with a 1.11 cm inner diameter and the air

flows from a 101.6 cm diameter outer tube. The methane velocity is 10.24 cm/s and the air velocity is 11.94 cm/s.

The ethylene co-flow flame model builds on the work done by Dworkin et al. [3]. That work uses experimental results of Köylü et al. [26] among others. As in the methane case, the Santoro [28] burner is used. The ethylene velocity is 3.98 cm/s and the air velocity is 8.9 cm/s.

The ethane co-flow flame is based on the work of Mandatori and Gülder [27]. A concentric annular burner that is capable of operating at pressures up to 33 atm is used. The inner fuel tube has an outer diameter of 0.306 cm and the outer air tube has an inner diameter of 2.54 cm. The fuel velocity is 2.89 cm/s and the air velocity is 10.34 cm/s. The methane flame operates at a pressure of 2 atm.

2.2 Chemical mechanism.

The chemical mechanism [5] had been developed for PAH formation modeling in methane and ethylene laminar premixed flames and later it was successfully used by Dworkin et al. [3] and Slavinskaya et al. [4] for ethylene diffusion flames. In this work, the mechanism was modified based on updated literature review and the current understanding of PAH formation processes [6,7,29-32]. It is important to understand that a detailed simulation of PAH growth is computationally expensive and it is impossible to follow each of the intermediate species and reactions at the aromatic ring formation stages. Therefore, most investigators consider the lumped species and reactions for PAH formation kinetic modeling. The structural analogy is usually applied to the rate constant evaluation for larger aromatics, scaled by increasing collision frequencies, and assuming the limiting stage is the rearrangement of the structure to form a new aromatic ring.

The changes and additions to the mechanism are shown obtained on the base of a literature survey [2,29-32] in Table 1. The cyclopentadiene/cyclopentadienyl system was revised in

accordance with the works of Robinson & Linstedt [29] and Mebel et al. [33]. Reaction of cyclopentadienyl (CPDyl) radical recombination in conjunction with molecular hydrogen was excluded from present model as well as analogy reactions for larger aromatics. The updated reactions of CPDyl recombination are shown in Table 1, reactions 1-5. The new reaction steps leading via CPDyl to indenyl and styrene formation proceeding via H abstraction from CPD proposed by Mebel et al. [33] were adopted in the model, reactions number 3 and 5, Table 1.

Table 1. The changes to the chemical mechanism of Slavinskaya and Frank[5] made available online in [4]. Units are mol, cm³, s and K.

No.	Reaction	A	n	E _a	Ref.
<i>Reactions of cyclopentadienyl radical</i>					
1	2C5H5 => A2+2H	3.00E+16	0.0	23625.0	[29]
2	2C5H5 => A2+2H	4.53E+05	1.83	18041.0	[29]
3	C5H5+H2CCCH = A1C2H3	1.00E+16	0.0	4174.0	[29]
4	C5H5+H2CCCH = INDENE	1.00E+16	0.0	4174.0	[est.]
5	2C5H5 = INDENYL+CH3	2.50E+12	.00	4811.0	[29]
6	C5H6+CH3 = C5H5 + CH4	1.00E-01	4.00	0.0	[29]
7	C5H5+C5H6 = INDENE + CH3	9.63E+13	Jan 63	29972.0	[29,30]
<i>Updated reactions analogous to cyclopentadienyl radical recombination</i>					
8	n-C8H7+A1C2H- => A4+2H	3.00E+17	.00	23625.0	
9	INDENYL+C5H5 => A3+2H	3.00E+17	.00	23625.0	
10	2INDENYL => C18H12+2H	6.00E+17	.00	23625.0	
11	A1C2H3*+A1C2H- = A4+2H	6.00E+17	.00	23625.0	
12	A2C2H*+n-C8H7 = BAPYR+2H	6.00E+17	.00	23625.0	
13	A2C2H*+A1C2H3* = BAPYR+2H	6.00E+17	.00	23625.0	
14	A2R5-+A1- => BGHIF+2H	6.00E+17	.00	23625.0	
15	P2-+A1C2H- => BAPYR+2H	6.00E+17	.00	23625.0	

<i>Added reactions of PAH with CH3 radical</i>					
16	$A1C2H3 + CH3 = A1C2H3^* + CH4$	2.00E+15	.00	7530.0	[31]
17	$A2R5 + CH3 = A2R5 + CH4$	2.00E+15	.00	7530.0	[31]
18	$P2 + CH3 = P2 + CH4$	2.00E+15	.00	7530.0	[31]
19	$A1C2H3^* + CH3 = INDENE + 2H$	3.00E+21	.00	36500.0	[32]
<i>Added abstraction steps</i>					
20	$A1 + O = C5H6 + CO$	5.80E+19	-0.77	7645.0	[7]
21	$A2R5 + OH \Rightarrow A2 + HCCO$	1.76E+05	3 25	2795.2	[7]

Reaction number 4 was estimated as a global step providing a pathway to indene, analogous to Reaction 3 from Robinson and Lindstedt [29]. Reactions 8-15 were estimated as a global step, analogous to $C_5H_5 + C_5H_5 = A_2 + H + H$ in Robinson and Lindstedt [29], with increased collision efficiency. The values of the reactions 16-18 were adjusted as analogous to the rate coefficient for $A_1 + CH_3 = A_1^* + CH_4$ given by Fournet et al. [31]. Reaction 19 was estimated as a global step providing a pathway to indene, analogous to $INDENYL + CH_3 = A_2 + H + H$ given by Laskin and Lifshitz [32]. The mechanism files can be found in the supplementary material.

2.3 Co-flow flame soot model description.

The Parallel CoFlame Code was used in the present work, for which the computational approach, soot model, and numerical algorithm are described in detail elsewhere [3,15,16]. The axial symmetry of the burner allows use of a two dimensional (z and r) coordinate system. For the gaseous phase, fully coupled elliptical conservation equations for mass, energy and species mass fractions are solved. Soot particle dynamics are described using a sectional model. Soot particle mass ranges are divided logarithmically into 35 discrete sections. Soot aggregates are composed of primary particles of equal size with a constant fractal dimension of 1.8 and are

divided to 35 sections for primary particle number in the aggregate. Thus, conservation equations of soot aggregate number densities and primary particle number densities are solved. The nucleation of a soot particle is modeled on the collision of two pyrene molecules [1]. The surface growth is implemented using the HACA mechanism and through PAH condensation. Radiative heat transfer by soot, H_2O , CO_2 , and CO is calculated using the discrete-ordinates method and a statistical narrow-band correlated- k -based model [34]. Oxidation, coagulation, and fragmentation are also included in the model.

Symmetry and zero-gradient conditions are enforced at the centreline and the outflow boundary conditions, respectively. For consistency with the experimental conditions, at the outer radial boundary a free-slip condition is used for the methane and ethylene flames and a no-slip condition is used for the ethane flame. The flame is solved using distributed-memory parallel processing, with the computational domain divided uniformly into 192 subdomains with the boundaries of each subdomain perpendicular to the z -axis.

3 Results and discussion.

3.1 Gas phase mechanism performance in premixed flames.

Before using the revised model, it is important to make sure that the model produces acceptable predictions for gas phase reactions. The proposed modifications slightly improve the agreement of methane and ethylene premixed laminar flame simulations with experimental results demonstrated in [4,5] and will not be presented here. The results that are shown were computed for methane and ethane premixed flames.

Figure 1 compares the ethane/air laminar flame speed computed using the current model with experimental results of Egolfopoulos et al. [35], Bosschaart and De Goey [36], and Jomaas et al. [37]. It can be seen that the computed values of flame speeds show good agreement with the

experimental measurements, with differences being about no more than 2–3 cm/s greater than the experimental data.

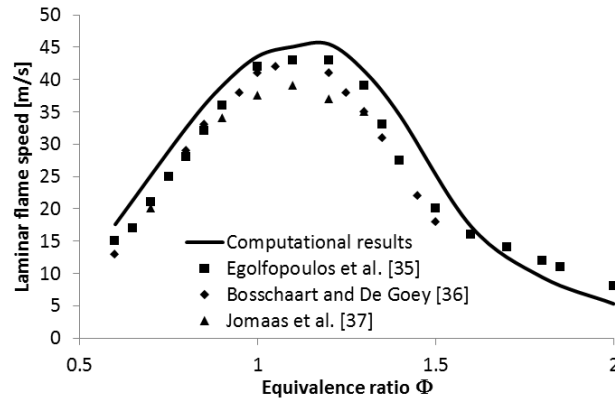


Figure 1. Ethane/air laminar flame speed. The solid line is the computed result, the symbols are experimental results [35-37].

Temperature measurement uncertainties can greatly influence concentration measurements in burner stabilized premixed laminar flames. Authors of experimental data selected for the model validation [22-24] report temperature uncertainties up to 100 K. Figure 2(a) shows the sensitivity of the computed indene concentrations to the temperature uncertainty in a premixed ethane/oxygen flame [22]. The temperature profiles are shown in Figure 2(b): the solid lines show the calculated indene concentration and the temperature reported by Melton et al. [22]; the dashed lines show the computed indene concentration if thermocouple radiation losses are included and the temperature corrected accordingly [5]; and the dotted lines show the computed indene concentration for reported temperatures reduced by 100 degrees, i.e. by supplied temperature uncertainty [22]. It can be clearly seen that changes within the reported temperature uncertainties can change indene concentrations by two orders of magnitude. It can also be seen that for some temperatures, an atypical minimum is present at approximately $h = 5$ mm. This minimum diminishes if the temperature that is used for calculation was lower by 100 degrees than reported by Melton et al. [22]. The atypical minimum on the concentration profiles is caused by the equilibrium shift in some reactions at enhanced temperatures. This situation

requires a careful choice of the temperature for the calculations. Therefore, the temperatures for simulations were reduced (keeping the value in the given uncertainty boundaries [22-24]) by 40-60K to produce more reliable concentration profile.

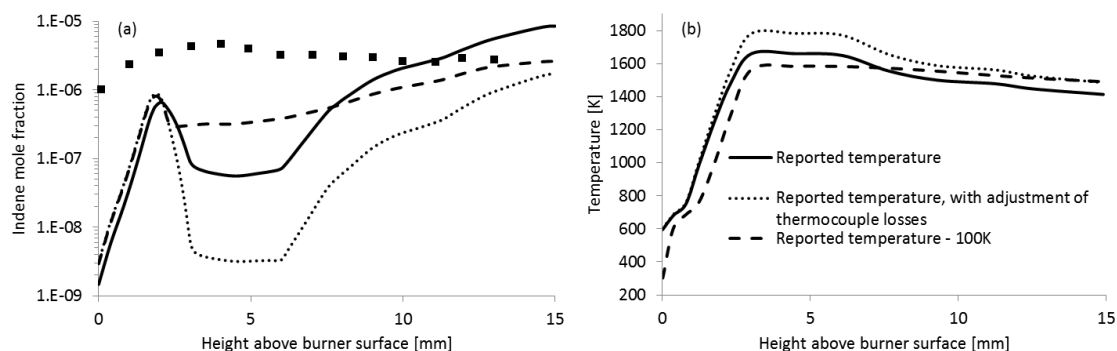


Figure 2. (a) Computed (lines) indene concentrations for various temperature profiles compared with experimental measurements (symbols) in ethane/oxygen co-flow flame [22]. (b) The temperature profiles used.

The model abilities to reproduce the measured soot precursors in methane and ethylene laminar flames were demonstrated in previous works [3-5] in details. The modifications and improvements shown in Table 1, i.e. corrected cyclopentadiene/cyclopentadienyl chemistry and added methyl addition mechanism, resulted in a better agreement with experimental data presented in [3-5] and led to an increase of 2 times compared to simulations [5] in predictions of pyrene concentrations in methane flames.

Figure 3 shows the acetylene and ethylene concentrations in the methane/oxygen premixed flame measured by Afle et al. [23]. It can be seen that the computations (lines) are close to the measurements (symbols) in both cases, though in the acetylene case the computed peak is located lower in the flame than it was measured. The discrepancy, however, is small and the quality of the predictions is satisfactory.

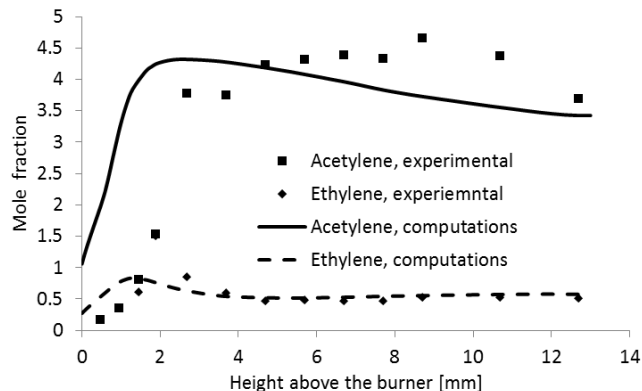


Figure 3. Computed (lines) and measured (symbols) concentrations of acetylene and ethylene for methane/oxygen premixed flame by Afle et al. [23]

Figure 4(a) shows the methane, acetylene and ethylene concentrations in ethane/oxygen premixed flame measured by Castaldi et al. [24]. It can be seen that the methane computed concentrations follow in a good manner the measurements for most of the flame; the acetylene computed concentrations also are in a good agreement with the measurements up to $h = 6$ mm and the ethylene computed concentrations are spatially shifted by about 1 mm, but provide good quantitative predictions. Figure 4(b) shows the large PAH molecules for the same flame. It can be seen that the computed concentration profile of pyrene is shifted by about 0.5 mm, but provides a good quantitative prediction. Other species concentration profiles show lesser agreement with the measurements, however for the needs of the current model, where pyrene is the main soot precursor, the results are sufficiently accurate.

Figure 5(a) show the methane, ethylene, and acetylene concentrations in ethane/oxygen premixed flame measured by Melton et al. [22]. It can be seen that the computed concentration profiles agree well with the measured ones. Especially this is true for acetylene, which is the central growth species in this model. Figure 5(b) shows that higher in the flame the soot precursor for the model, pyrene, is predicted well. In general, it can be seen that soot precursors are predicted well for three different premixed datasets.

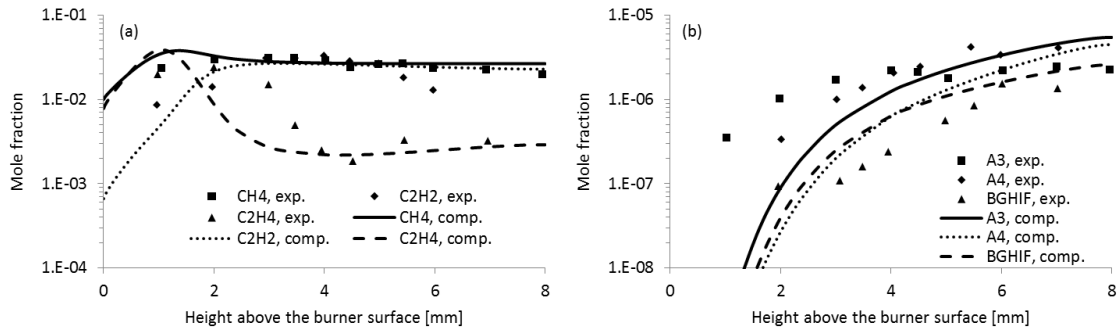


Figure 4. Computed (lines) and measured (symbols) concentrations of (a) selected light hydrocarbons and (b) selected PAHs for $C_2H_6/O_2/Ar$ premixed flame by Castaldi et al. [24], $p = 1\text{bar}$, $\phi = 2.6$.

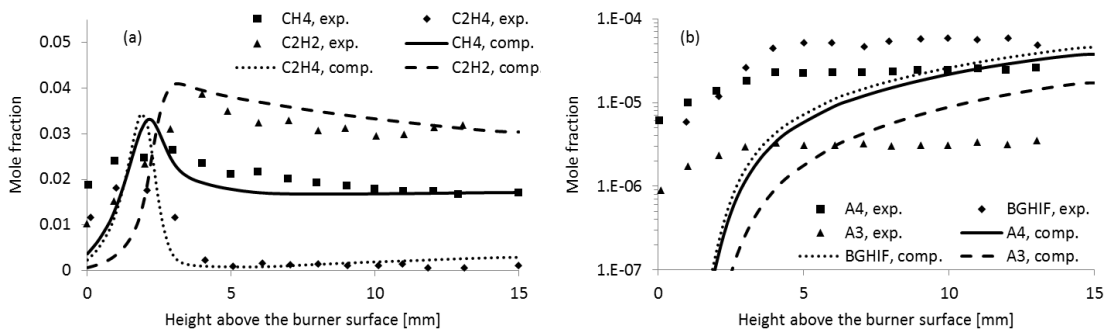


Figure 5. Computed (lines) and measured (symbols) concentrations of (a) selected light hydrocarbons and (b) selected PAHs for $C_2H_6/O_2/Ar$ premixed flame by Melton et al. [22], $p = 1\text{bar}$, $\phi = 2.6$.

One of the aims of introducing the original mechanism by Slavinskaya and Frank [5] was to improve the accuracy of the chemical mechanism in predicting PAH soot precursors creation in the PAH-dominated centerline of the flame. While Dworkin et al. [3] showed improvement for the centerline result of ethylene/air co-flow diffusion flame, this improvement has not been observed in the initial calculations of methane/air co-flow diffusion flame. As a result, the changes in Section 2.3 were introduced. After the changes were implemented, it was important to make sure that the soot precursors in the other cases are not adversely influenced by the change. In our model, pyrene is considered as the main aromatic precursor to soot formation, representing all aromatics in both inception and condensation. Figure 6 shows the profiles of pyrene mole fraction computed using the original mechanism [3] (solid line) and using the present work additions (dashed line). It can be seen that in the case of the methane co-flow

flame [25] (left hand side) the differences in pyrene concentrations are on the order of up to 200% (noting the log scale), while in the case of the ethylene co-flow flame [26] (right hand side), the differences are very small. It can also be seen that the new mechanism additions and changes fulfill the aim of boosting the amount of pyrene in the system, which (together with good performance shown previously) makes the changes desirable.

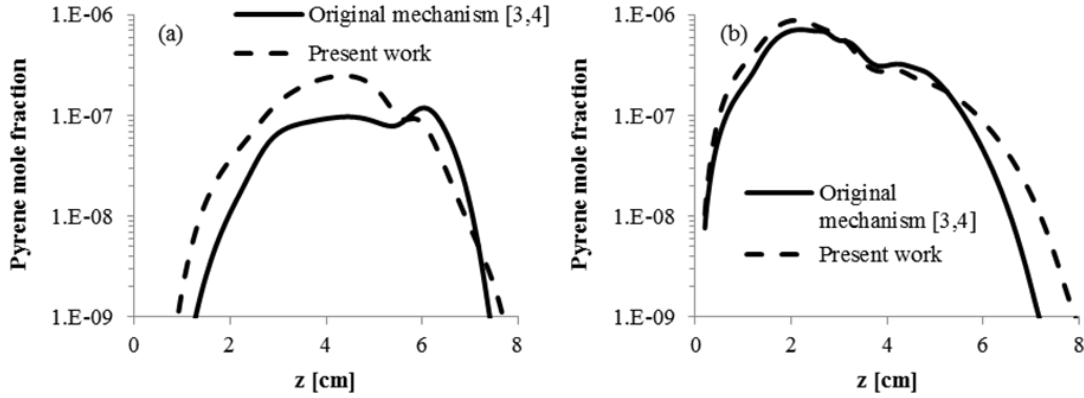


Figure 6. Computed pyrene mole fractions along the centerline for (a) methane [25] and (b) ethylene co-flow diffusion flames [26]. The solid line represents the results using the original mechanism used by Dworkin et al. [3] and Slavinskaya et al. [4]; the dashed line represents the results obtained by the changes shown in Section 2.3.

3.2 Soot model performance for the co-flow flames.

The first computational result to be examined is the maximum soot volume fraction. Maximum soot volume fraction is of interest both from an emissions point of view and mechanical design point of view. Figure 7 shows the computed maximum soot volume fractions compared to the experimental data for all the three co-flow diffusion flames. The experimental data is presented as a range of values according to the estimated experimental uncertainty. Lee et al. [25] do not report the uncertainty for the methane experiments, but 30% uncertainty is reported in the literature [38] for the LOSA technique used by Lee et al. [25]; Mandatori and Gülder [27] report 30% uncertainty, and Köylü et al.[26] - 35%. It can be seen that while the computed maximum soot volume fraction is within the error bar range for methane, the maximum soot volume fractions of ethane and ethylene co-flow flames are slightly out of the experimental uncertainty

range. However, all of the computational results are within factor of two of the experimental results. It can also be seen that the model provides reasonable results over a wide range of soot volume fractions; the measured soot volume fractions vary by about two orders of magnitude, yet the model results lie outside of the experimental uncertainty only slightly, if at all. In fact, in this case, the error bars are only estimated, and in reality may be larger. This result demonstrates the robustness of the model as applied to predicting peak soot volume fractions.

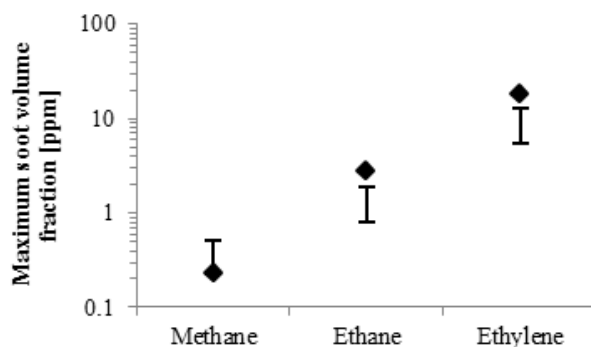


Figure 7. Maximum soot volume fractions for co-flow diffusion flames of different fuels. The symbols are computations, the bars are the experimental data [25-27] within the uncertainty range.

Observing individual results for each co-flow flame can show more details from the model. The next figures show the results for each individual flame. Figure 8 shows the soot volume fractions for the methane co-flow flame along the path of maximum soot, which is found on the wings of the flame. The dashed line represents the computational results obtained using the mechanism used by Dworkin et al. [3], the solid line represents the computational results obtained using the enhanced version of the mechanism described in Section 2.3 of the present work, and the symbols represent the experimental data [25]. It can be seen that the current predictions of the soot volume fraction are close to the experimental data and are in fact within experimental uncertainty (error bars not shown). Also, it can be seen the previous version of the mechanism under-predicts the experimental results by an order of magnitude. This shows that the

enhancement shown in Section 2.3 improved the prediction quality significantly. In addition, the location of the maximum soot point, and the overall trend in the profile are well reproduced.

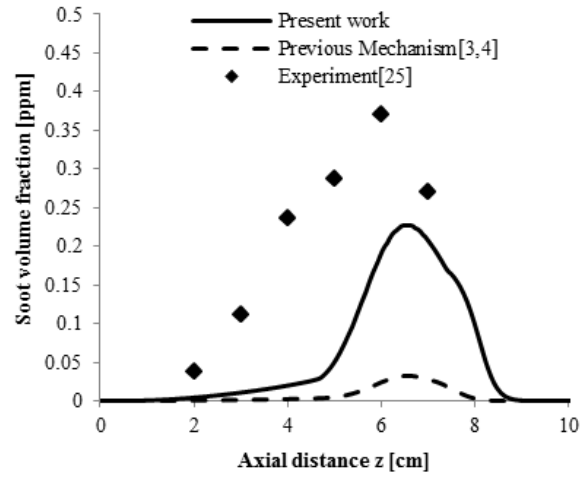


Figure 8. Soot volume fractions along the path of maximum soot for the methane co-flow flame [25].

A similar trend can be seen in Figure 9 that shows the soot volume fractions along the normalized centerline. The centerline was normalized by the location of maximum soot as has been done in previous studies [13,39]. The normalization is necessary since the computations of the flame height are inexact. As can be seen, the model went from under-prediction of an order of magnitude in the previous version of the mechanism to being within a factor of two with the current mechanism version.

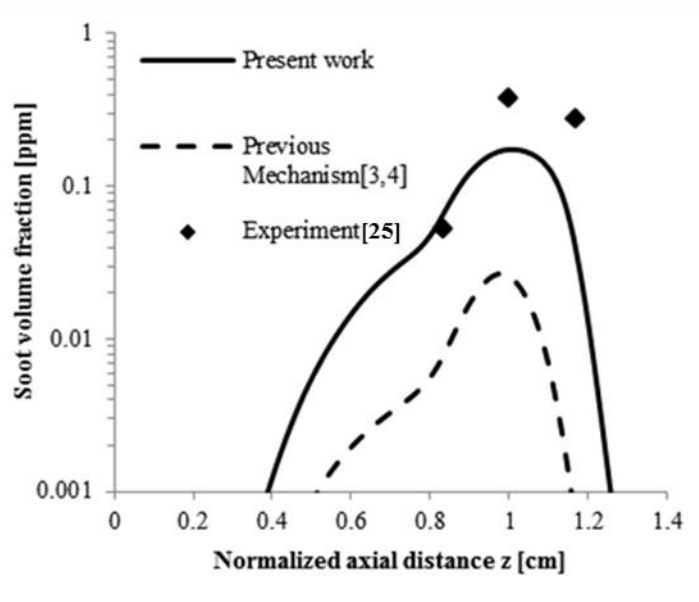


Figure 9. Soot volume fractions along the centerline the co-flow methane flame [25].

Figure 10 shows the current computational results for the soot volume fraction along the centerline and maximum soot path in the ethylene co-flow flame compared with experimental data [26], and with predictions of Dworkin et al. [3]. The centerline results in Figure 10(a) show that in the lower part of the flame, the enhanced model provides slightly better predictions than that of Dworkin et al. [3]. Both models under-predict the soot volume fraction in the upper part of the flame but are within the correct order of magnitude. Dworkin et al. [3] showed that the soot on the centerline is PAH-dominated and is strongly linked to the gas phase aromatic chemistry. The fact that the soot predictions on the centerline have not changed significantly between the current work and that of Dworkin et al. [3] is an additional evidence that while the mechanism changes that are presented in Section 2.3 improve the methane computations, they do not worsen the ethylene centerline computations. The maximum soot path results in Figure 10(b) show that for the low part of the flame ($z < 4$ cm), the current model over-predicts the soot volume fractions by about a factor of two. Since Figure 6 and Figure 10(a) show that the change in the gas-phase chemistry has a negligible influence on the soot volume fraction results,

the difference between the computational results in this work and the work of Dworkin et al. [3] in Figure 10(b) is due to the parameter α being higher in the present work.

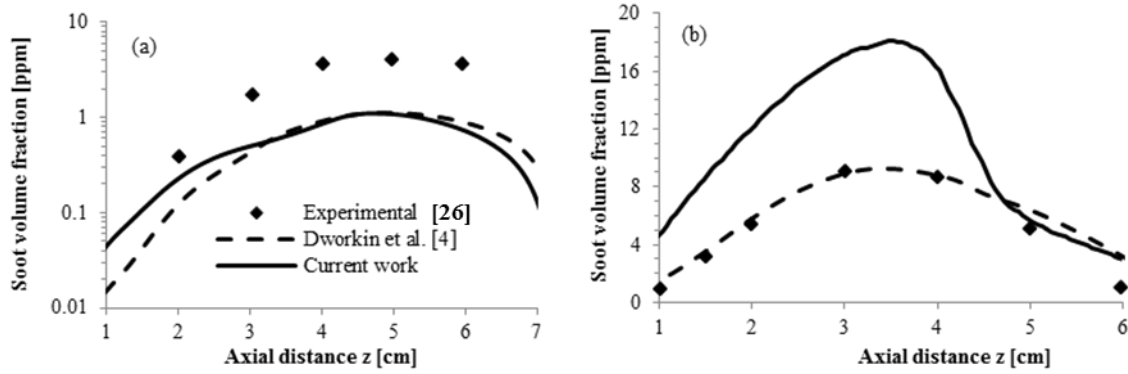


Figure 10. Soot volume fractions for (a) centerline and (b) path of maximum soot for the co-flow ethylene flame.

Figure 11 shows the soot volume fractions along the maximum soot path of the ethane co-flow flame [27]. The computations are shown by the solid line and the experimental results by the symbols. It can be seen that soot along the maximum soot path is, similar to the ethylene case, over-predicted by a factor of two. The axial location of the point of maximum soot is well predicted.

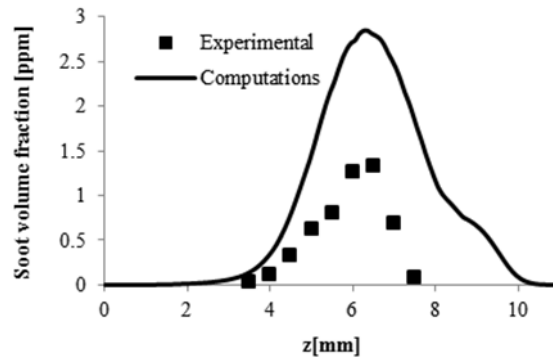


Figure 11. Soot volume fraction along the maximum soot path for the co-flow ethane flame. The experimental results are from Mandatori and Gülder [27].

Figure 12 shows the soot volume fractions along the normalized centerline of the ethane flame [27]. It can be seen that centerline soot formation computation is again within a factor of two

from the measurements. The centerline soot volume fractions are in many cases more difficult to predict [3] and a relatively small under-prediction can be considered a very good result.

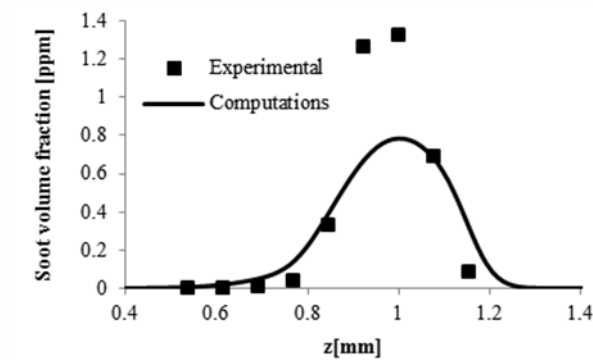


Figure 12. Soot volume fraction along the normalized centerline for the ethane co-flow flame. The experimental results are from Mandatori and Gülder [27].

3.3 Comparison of methane and ethylene co-flow flames.

The ethylene [26] and methane [27] co-flow flames that were chosen as experimental data sources share some common aspects. Both use the same Santoro burner [28]; the computed flame heights are also similar - $H_T = 7.9$ cm for the methane flame and $H_T = 7.2$ cm for the ethylene flame (the flame height is determined by the location of maximum temperature on the centerline of the burner). Therefore comparing them in more detail allows for a good understanding of the performance of the soot model across flames of different fuels.

One species that is of major interest in the sooting flame analysis is acetylene. Acetylene addition through HACA is one of the two dominant soot growth mechanisms (the other is PAH condensation [1]). Figure 13 shows the computed acetylene mole fractions along the path of maximum soot for methane (solid line) and ethylene (dashed line) co-flow flames. The x axis shows the axial distance normalized by the flame height. As expected, it can be seen that acetylene behaves in a very different manner for the two cases. In the ethylene case there is a sharp rise and fall of acetylene concentration, whereas in the methane case the acetylene concentration remains near its peak level over most of the flame height ($0.1 < z/H_T < 0.6$).

Acetylene is formed directly during ethylene decomposition whereas with methane it requires formation of methyl radical followed by radical recombination.

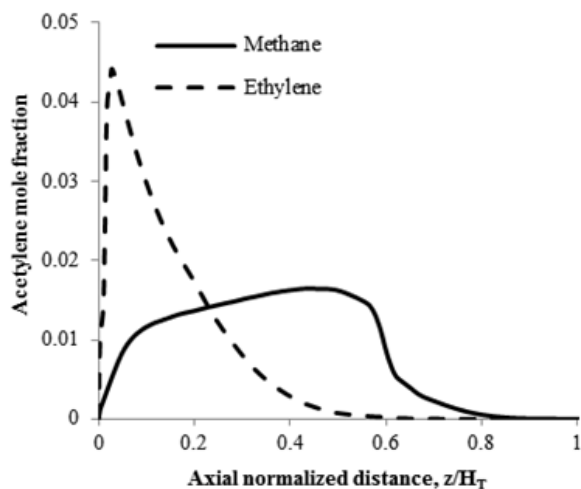


Figure 13. Computed acetylene mole fraction along the path of maximum soot for methane and ethylene co-flow flames.

The soot growth is also different for the two flames. Figure 14 shows the contributions of the inception, HACA surface growth and PAH condensation to the soot mass addition along the maximum soot path for methane and ethylene co-flow flames. The plots are normalized by the maximum soot mass addition. The oxidation of the soot particles is not shown. It can be seen that soot formation in the two flames exhibits different soot growth dynamics. For example, the soot growth in the methane flame starts much further away from the burner relative to the ethylene flame. Figure 13 and Figure 14 show that the two flames with similar macro-properties (burner configuration and flame height) exhibit considerable differences in molecular profiles and overall character when examined more closely.

Furthermore, it can be seen that in the ethylene co-flow flame, due to much higher acetylene levels, inception contributes a much smaller portion of the soot mass than in the methane co-flow flame. This might be one of the reasons as to ethylene, and not methane, being the fuel of choice in many soot modeling studies. In ethylene flames, inception was less important and if

surface growth could be accurate, then soot concentrations could be relatively accurate. On the other hand, the methane flame, is considerably more dependent on accurate soot precursor prediction and therefore more accurate gas phase PAH mechanism is a vital step for improving the quality of the soot prediction.

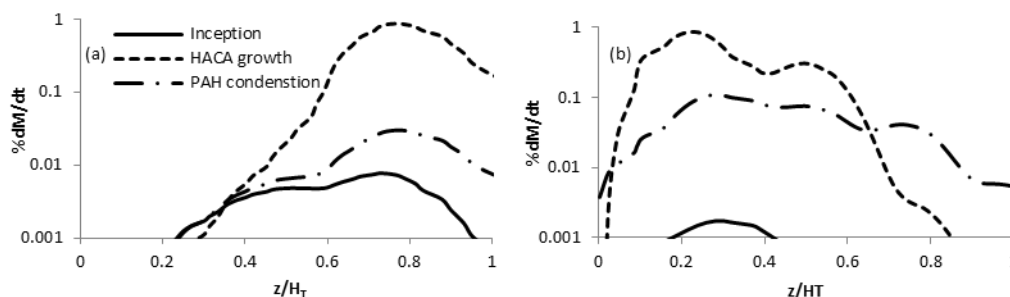


Figure 14. Computed normalized factors of soot growth along the path of maximum soot for a) methane and b) ethylene co-flow flames.

4 Conclusions.

Modifications to a gas phase chemical mechanism are proposed to increase the quality of the prediction of soot precursors in methane co-flow flames without decreasing the quality of these predictions for ethylene co-flow flames. The goals were to see whether the changes would provide good predictions for gas phase species, to make sure that the predictions for other fuels would not be worsen by the changes, to test applicability of the soot prediction setup across several fuels and to assess its robustness. Several conclusions can be drawn.

In the case of the mechanism verification, the prediction of the concentration of soot precursors such as acetylene and pyrene in the premixed cases was satisfactory. These datasets have not been simulated before and a good prediction of soot precursors, along with increased accuracy prediction for previously simulated datasets provided a solid foundation for a complex soot simulation. The changes also were found to increase the production of PAHs in the methane/air co-flow diffusion flame, while having little impact in the case of ethylene/air flames. This

confirms that the changes introduced to the mechanism were an upgrade, with very little (if at all) undesirable side-effects.

It was found that the soot calculations algorithm, with the addition of the changes in the gas-phase mechanism, performs robustly in varying conditions. Three different co-flow datasets were simulated, with the ethane set being a smaller burner of the other two and the maximum soot volume fraction changed in two orders of magnitudes between the sets. Still, the computed maximum volume fractions were within a factor of two for all cases, with the new additions to the mechanism clearly contributing to this.

The main improvement in soot prediction was observed for the methane/air co-flow flames. The reason for this improvement was found to be the nature of the soot behavior in methane flames. It was found that the soot inception process plays a more important role in the case of methane than in the case of ethylene co-flow flame, not only on the centerline (where the inception is the dominant process of soot growth), but also on the path of maximum soot. Therefore, the mechanism changes, despite being motivated by centerline processes, greatly influence the whole flame region.

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Reference List

- [1] J. Appel, H. Bockhorn, M. Frenklach, Kinetic modeling of soot formation with detailed chemistry and physics: laminar premixed flames of C₂ hydrocarbons, *Combust. Flame.* 121 (2000) 122-136.
- [2] H. Wang, M. Frenklach, A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames, *Combust. Flame.* 110 (1997) 173-221.
- [3] S.B. Dworkin, Q. Zhang, M.J. Thomson, N.A. Slavinskaya, U. Riedel, Application of an enhanced PAH growth model to soot formation in a laminar coflow ethylene/air diffusion flame, *Combust. Flame.* 158 (2011) 1682-1695.
- [4] N.A. Slavinskaya, U. Riedel, S.B. Dworkin, M.J. Thomson, Detailed numerical modeling of PAH formation and growth in non-premixed ethylene and ethane flames, *Combust. Flame.* 159 (2011) 979-995.
- [5] N. Slavinskaya, P. Frank, A modelling study of aromatic soot precursors formation in laminar methane and ethene flames, *Combust. Flame.* 156 (2009) 1705-1722.
- [6] A. Raj, M. Celnik, R. Shirley, M. Sander, R. Patterson, R. West, M. Kraft, A statistical approach to develop a detailed soot growth model using PAH characteristics, *Combust. Flame.* 156 (2009) 896-913.
- [7] K. Narayanaswamy, G. Blanquart, H. Pitsch, A consistent chemical mechanism for oxidation of substituted aromatic species, *Combust. Flame.* 157 (2010) 1879-1898.
- [8] B. Shukla, M. Koshi, A highly efficient growth mechanism of polycyclic aromatic hydrocarbons, *Phys.Chem.Chem.Phys.* 12 (2010) 2427-2437.
- [9] M. Di Domenico, P. Gerlinger, M. Aigner, Development and validation of a new soot formation model for gas turbine combustor simulations, *Combust. Flame.* 157 (2010) 246-258.

- [10] F. Gelbard, J.H. Seinfeld, Simulation of multicomponent aerosol dynamics, *J. Colloid Interface Sci.* 78 (1980) 485-501.
- [11] F. Gelbard, Y. Tambour, J.H. Seinfeld, Sectional representations for simulating aerosol dynamics, *J. Colloid Interface Sci.* 76 (1980) 541-556.
- [12] C.S. McEnally, L.D. Pfefferle, Soot formation in methane/air nonpremixed flames doped with small quantities of C_3 hydrocarbons, *Combust. Flame.* 112 (1998) 545-558.
- [13] M. Smooke, M. Long, B. Connelly, M. Colket, R. Hall, Soot formation in laminar diffusion flames, *Combust. Flame.* 143 (2005) 613-628.
- [14] S. Dworkin, M. Smooke, V. Giovangigli, The impact of detailed multicomponent transport and thermal diffusion effects on soot formation in ethylene/air flames, *Proceedings of the Combustion Institute.* 32 (2009) 1165-1172.
- [15] Q. Zhang, M. Thomson, H. Guo, F. Liu, G. Smallwood, A numerical study of soot aggregate formation in a laminar coflow diffusion flame, *Combust. Flame.* 156 (2009) 697-705.
- [16] Q. Zhang, H. Guo, F. Liu, G. Smallwood, M. Thomson, Modeling of soot aggregate formation and size distribution in a laminar ethylene/air coflow diffusion flame with detailed PAH chemistry and an advanced sectional aerosol dynamics model, *Proceedings of the Combustion Institute.* 32 (2009) 761-768.
- [17] M. Saffaripour, P. Zabeti, S. Dworkin, Q. Zhang, H. Guo, F. Liu, G. Smallwood, M. Thomson, A numerical and experimental study of a laminar sooting coflow Jet-A1 diffusion flame, *Proceedings of the Combustion Institute.* 33 (2011) 601-608.
- [18] V. Chernov, Q. Zhang, M.J. Thomson, S.B. Dworkin, Numerical investigation of soot formation mechanisms in partially-premixed ethylene–air co-flow flames, *Combust. Flame.* 159 (2012) 2789-2798.

- [19] N.A. Eaves, A. Veshkini, C. Riese, Q. Zhang, S.B. Dworkin, M.J. Thomson, A numerical study of high pressure, laminar, sooting, ethane–air coflow diffusion flames, *Combust. Flame*. 159 (2012) 3179-3190.
- [20] G. Blanquart, H. Pitsch, Analyzing the effects of temperature on soot formation with a joint volume-surface-hydrogen model, *Combust. Flame*. 156 (2009) 1614-1626.
- [21] T. Blacha, M. Di Domenico, P. Gerlinger, M. Aigner, Soot predictions in premixed and non-premixed laminar flames using a sectional approach for PAHs and soot, *Combust. Flame*. 159 (2012) 181-193.
- [22] T.R. Melton, F. Inal, S.M. Senkan, The effects of equivalence ratio on the formation of polycyclic aromatic hydrocarbons and soot in premixed ethane flames, *Combust. Flame*. 121 (2000) 671-678.
- [23] M. Alfè, B. Apicella, J.N. Rouzaud, A. Tregrossi, A. Ciajolo, The effect of temperature on soot properties in premixed methane flames, *Combust. Flame*. 157 (2010) 1959-1965.
- [24] M.J. Castaldi, S.M. Senkan, PAH formation in the premixed flame of ethane, *Combustion Sci. Technol.* 116 (1996) 167-181.
- [25] K.O. Lee, C.M. Megaridis, S. Zelepouga, A.V. Saveliev, L.A. Kennedy, O. Charon, F. Ammouri, Soot formation effects of oxygen concentration in the oxidizer stream of laminar coannular nonpremixed methane/air flames, *Combust. Flame*. 121 (2000) 323-333.
- [26] Ü.Ö. Köylü, C. McEnally, D. Rosner, L. Pfefferle, Simultaneous measurements of soot volume fraction and particle size/microstructure in flames using a thermophoretic sampling technique, *Combust. Flame*. 110 (1997) 494-507.
- [27] P.M. Mandatori, Ö.L. Gülder, Soot formation in laminar ethane diffusion flames at pressures from 0.2 to 3.3 MPa, *Proceedings of the Combustion Institute*. 33 (2011) 577-584.

- [28] R. Santoro, H. Semerjian, R. Dobbins, Soot particle measurements in diffusion flames, *Combust. Flame*. 51 (1983) 203-218.
- [29] R. Robinson, R. Lindstedt, On the chemical kinetics of cyclopentadiene oxidation, *Combust. Flame*. 158 (2011) 666-686.
- [30] R.G. Butler, Combustion Chemistry of 1, 3-cyclopentadiene. (2001), Ph.D. Thesis, Department of Chemistry, Princeton University, Princeton, New Jersey, USA.
- [31] R. Fournet, J. Baugé, F. Battin-Leclerc, Experimental and modeling of oxidation of acetylene, propyne, allene and 1, 3-butadiene, *Int J Chem Kinet*. 31 (1999) 361-379.
- [32] A. Laskin, A. Lifshitz, Thermal decomposition of indene. Experimental results and kinetic modeling, *Symposium (International) on Combustion*. 27 (1998) 313-320.
- [33] A. Mebel, V. Kislov, Can the $C_5H_5 + C_5H_5 \rightarrow C_{10}H_{10} \rightarrow C_{10}H_9 + H/C_{10}H_8 + H_2$ Reaction Produce Naphthalene? An Ab Initio/RRKM Study, *The Journal of Physical Chemistry A*. 113 (2009) 9825-9833.
- [34] F. Liu, H. Guo, G.J. Smallwood, Effects of radiation model on the modeling of a laminar coflow methane/air diffusion flame, *Combust. Flame*. 138 (2004) 136-154.
- [35] F. Egolfopoulos, D. Du, C. Law, A study on ethanol oxidation kinetics in laminar premixed flames, flow reactors, and shock tubes, 24 (1992) 833-841.
- [36] K.J. Bosschaart, L. De Goey, The laminar burning velocity of flames propagating in mixtures of hydrocarbons and air measured with the heat flux method, *Combust. Flame*. 136 (2004) 261-269.
- [37] G. Jomaas, X. Zheng, D. Zhu, C. Law, Experimental determination of counterflow ignition temperatures and laminar flame speeds of C_2 - C_3 hydrocarbons at atmospheric and elevated pressures, *Proceedings of the Combustion Institute*. 30 (2005) 193-200.

[38] K.A. Thomson, Soot Formation in Annular Non-Premixed Laminar Flames of Methane-Air at Pressures of 0.1 to 4.0 MPa, (2006) Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada.

[39] B.A.V. Bennett, C.S. McEnally, L.D. Pfefferle, M.D. Smooke, M.B. Colket, Computational and experimental study of the effects of adding dimethyl ether and ethanol to nonpremixed ethylene/air flames, *Combust. Flame*. 156 (2009) 1289-1302.