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Pradeep Singh and Chih-Jen Sung
Department of Mechanical Engineering
University of Connecticut
Storrs, CT 06269, USA

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Corresponding Author:

Chih-Jen Sung
Department of Mechanical Engineering
University of Connecticut
Storrs, CT 06269, USA
Email: chih-jen.sung@uconn.edu

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Department of Mechanical Engineering
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Abstract

Using the planar laser-induced fluorescence (PLIF) technique in a counterflow non-premixed flame configuration, the formation of the polycyclic aromatic hydrocarbons (PAHs) for the butane isomers and the butanol isomers was investigated. For these C₄ fuels, the PAHs of various aromatic ring size groups (2, 3, 4, and larger aromatic rings) have been characterized and compared in non-premixed combustion configuration. In particular, the formation and growth of the PAHs of different aromatic ring sizes in these counterflow flames was examined by tracking the PAH-PLIF signals at various detection wavelengths. The fuel structure effects on the PAH formation and growth processes were also analyzed by comparing the PAH growth pathways for these C₄ fuels. Furthermore, PAH-PLIF experiments were conducted, by blending each of the branched-chain isomers with the baseline straight-chain isomer, in order to study the synergistic effects, as well as identify the relative importance of the H-abstraction-C₂H₂-addition (HACA) mechanism and the propargyl (C₃H₃) recombination/addition pathways in the PAH formation and growth processes. A chemical kinetic model available in the literature that includes both the fuel oxidation and the PAH chemistry was also used to simulate and compare the PAH species up to A₄ rings. At the incipient stage of the PAH formation, the simulated results exhibited similar behavior to the experimental observations. The PAH formation pathways considered in the chemical kinetic model were further analyzed. In addition to propargyl, the present results demonstrated the important role of acetylene in the PAH formation and growth processes.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the precursors in the soot formation process in combustion [cf. 1-4]. The PAHs and soot are known to be harmful to the environment and human health. The PAHs can be generated by various sources such as in the internal combustion engines used for transportation and in the combustors used for power generation, as a result of incomplete combustion. The regulatory measures over the time have become more stringent to reduce the particulate emissions from the engines and the combustors. Moreover, the design of modern combustion engines and devices requires understanding the fundamental PAH/soot formation and growth chemistry to achieve this goal.

Numerous studies on the PAH formation in flames have been conducted by a number of groups [e.g., 5-9]. The PAH concentration measurements have been performed by direct sampling and gas chromatograph/mass spectrometer (GC/MS) analysis of fuel-rich, laminar premixed flames [5]. In addition, two-photon ionization time-of-flight mass spectroscopy has been used to analyze the PAHs from laminar non-premixed flames [6]. Shock tube data at elevated pressures have been evaluated to predict the reaction pathways for the PAHs [7]. Using an online GC/MS technique, the PAH formation has been investigated in a fuel-rich, premixed, sooting burner stabilized flame for *n*-butane [8]. Molecular-beam-mass-spectrometry (MBMS) coupled with resonance-enhanced-multi-photon-ionization (REMPI) techniques have been employed to measure the concentrations of the small PAHs up to 3 aromatic rings in fuel-rich, premixed flames of propene and cyclopentene [9]. In general, the motive behind the above-mentioned studies was to provide the experimental database to build the reaction pathways for the PAH and soot formation processes.

The widely accepted H-abstraction-C₂H₂-addition (HACA) mechanism of the PAH formation was proposed by Frenklach and coworkers [e.g., 10-15]. Apart from the HACA mechanism, the pathways involving propargyl, allyl, cyclopentadienyl, and indenyl have also shown to contribute to the PAH formation processes [cf. 16-24]. Recently, Schenk *et al.* [25] have proposed the methyl- and phenyl-addition pathways of the PAH formation. In addition, the odd-carbon-atom pathways have been introduced as possible reaction routes of the incipient PAH formation, as the propargyl has been proposed to produce reasonably stable benzene rings [26-30]. Numerical studies have suggested that the propargyl is also responsible for the PAH growth pathways via the propargyl addition and recombination reactions [30-32].

To develop the soot formation chemistry, understanding the PAH formation process is essential. It is observed that there is a lack of experimental databases of the PAHs to develop the comprehensive soot formation chemistry, even in comparative terms between fuels of the same isomeric class. Considering this, in the current study, *in-situ* PAH measurements using the *non-intrusive* planar laser-induced fluorescence (PLIF) technique in a counterflow non-premixed flame configuration have been conducted for the butane isomers and the butanol isomers, providing a qualitative comparison of PAH growth for the C₄ fuels investigated. Specifically, the C₄ fuels investigated in this study are *n*- and *iso*-butanes, as well as *n*-, *iso*-, *sec*-, and *tert*-butanols. The molecular structures of these fuels are shown in Table 1. By measuring the spatial locations of the PAH fluorescence signals and the evolution of PAHs [33-41] and through sampling investigations [42-46], the evidences, linking the PAH fluorescence to the PAH molecules, have been shown in these literature studies. Through the present PAH-PLIF experiments, we aim to study the effects of molecular structure and hydroxyl functional group on the PAH formation and growth processes. By detecting the PAH-PLIF signals at varying

wavelengths, PAHs of different aromatic ring sizes have been tracked. Due to the limitations of quantitative PAH-PLIF measurements, qualitative PAH-PLIF results for the butane isomers and the butanol isomers have been compared. Because of the fuel structural effects, competitive PAH growth pathways are expected to exist [26]. Hence, fuels in the same isomeric class tend to generate different amounts of PAHs. The competitive roles of the HACA and the C_3H_3 pathways in the PAH formation have also been investigated experimentally and computationally in this study, by blending a branched-chain isomer with the corresponding straight-chain isomer at varying blending percentages. When keeping the total fuel loading constant, the concentrations of the propargyl and the acetylene are expected to change as a result of the fuel blending, thereby inducing the competition between the HACA and the C_3H_3 pathways for the PAH formation.

Table 1 Chemical structures of butane and butanol isomers.

Fuel	<i>n</i> -Butane	<i>iso</i> -Butane	<i>n</i> -Butanol	<i>iso</i> -Butanol	<i>sec</i> -Butanol	<i>tert</i> -Butanol
Chemical Structure

In the following, the experimental facility and the optical diagnostic techniques adopted in this study will be described, and the computational flame model and the reaction mechanism used to simulate the experimental conditions will be specified. Subsequently, the present experimental results will be presented and discussed, followed by a comparison with the simulated results and reaction path analyses to identify the important pathways accounting for the PAH formation in the isomeric fuels and the binary fuel blends.

2. Experimental specifications

2.1. Counterflow burner facility

A counterflow flame burner assembly, flow control system, liquid fuel pump, mass flow controller, lasers, and intensified charged coupled diode (ICCD) camera were used in the present experiments. The burner assembly consisted of two opposed convergent flow nozzles with a diameter of 10 mm, and the gap between the two nozzles was 11 mm. Butane and butanol isomers fuels were used in the experiment. The flow rates of the butane isomers were controlled by mass flow controllers, while butanol isomers were introduced in the flow system using a high-pressure liquid pump. These liquid butanol isomers were injected into a prevaporizer along with the heated coflowing nitrogen to convert the liquid fuel into fine droplets, thereby facilitating a complete vaporization. Using electric heating tapes, the fuel lines were maintained at an appropriate temperature to ensure that there was no condensation of the liquid fuel. The mixture of nitrogen and vaporized/gaseous fuel was introduced from the bottom nozzle, while the mixture of oxygen and nitrogen was introduced from the top nozzle. Both the fuel stream and the oxidizer stream were maintained at 400 K temperature. Further details on this counterflow burner facility can be found in [47-49].

2.2. Optical diagnostic techniques

In each experiment, a planar counterflow non-premixed flame was established and the flame was shrouded with a nitrogen co-flow to isolate the flame from the ambience and stabilize the flame. Two optical diagnostic techniques were used to respectively measure the soot volume fraction profiles quantitatively and the PAH concentration distributions qualitatively. For the soot volume fraction measurements, the laser-induced incandescence (LII) technique was employed using the second harmonics (532 nm) of a Nd:YAG laser (Continuum Powerlite 8010), an ICCD camera

(PI-MAX 3), and cylindrical optics. The present LII setup and the associated light extinction (LE) techniques for calibration have been described and discussed previously in [49]. For the PAH measurements, planar laser-induced fluorescence (PLIF) technique was used, involving a Nd:YAG-pumped dye laser (Continuum ND 6000) and a UVT tracker, in addition to the equipments and instruments used for the LII measurements. The schematic for the present PAH-PLIF experimental setup is shown in Fig. 1. In the dye laser, the Rhodamine-590 dye was used, which has an emission peak wavelength at 560 nm. The grating in the dye laser was adjusted to 566 nm output, and then the UVT was used to frequency double the laser beam output from the dye laser to achieve a UV laser beam at 283 nm wavelength. Two UV cylindrical lenses, plano-concave ($f = -25$ mm) and plano-convex ($f = 300$ mm), were used to create a laser sheet.

Figure 1: Schematic of experimental setup of counterflow non-premixed flame with PAH-PLIF laser diagnostic technique.

Since a relatively low laser fluence for the PAH-PLIF measurements was maintained at 250 mJ/cm² to avoid the incandescence of soot particles [2], it circumvented the noise due to the soot incandescence in the PAH-PLIF signal. In both the LII and PAH-PLIF techniques, the laser sheet was passed through the centerline between two opposed nozzles. In the LII measurements, the

ICCD camera detected 450 nm signal that was part of the broadband radiation generated by the soot particles. Reasons to select the 450 nm detection wavelength for the LII experiments were delineated in [49]. Detection wavelengths of 334 nm, 400 nm, 450 nm, and 492 nm were used in the PAH-PLIF experiments. Further details on mapping these detection wavelengths to the aromatic ring sizes of PAHs will be discussed in due course. In both the LII and PAH-PLIF experiments, 3 sets of 20 images were averaged to take the measurements. In these experiments all the filters used for detection were narrow band-pass filters (FWHM = ± 10 nm), which ensured minimal interference in the detected signal due to the other noise sources. With the current optical setup, the spatial resolution was 0.0384 mm/pixel.

2.3. Planar laser induced fluorescence (PLIF) for the PAH measurements

Since the LII technique used here has been described in details elsewhere [49], the present focus is on the description of the PAH-PLIF technique for PAH measurements. The theoretical background behind the PAH-PLIF technique is as follows. The PAH molecules are known to have good absorption cross sections over a wide range of excitation wavelengths from UV to visible [50]. Upon absorbing the UV excitations provided by the lasers, these PAH molecules undergo ro-vibronic transitions from the electronic ground state (S_0) to electronic excited states (S_2 or higher). Then from these excited states, these PAH molecules relax to the electronic state S_1 by the internal conversion and the ro-vibrational relaxation processes. Further, these excited PAH molecules provide fluorescence by relaxing back to the ro-vibrational levels of S_0 [51,52]. In addition, the emission wavelength from an excited PAH molecule depends on the number of aromatic rings this molecule possesses, while the emission wavelength is larger for a molecule with higher number of aromatic rings [51-53]. It is also known that the emission characteristics of the PAH molecules do not vary for an excitation wavelength in the range of 265–297 nm [53].

Researchers have attempted to provide quantitative measurements for the PAHs with limited success, as it is difficult to make a spectral distinction between aromatics, with the same number of rings, but different chemical structures [52,54], due to the broadband nature of emission spectra from these PAHs.

The optical diagnostic technique adopted here for the PAH measurements faces challenge as the signals of the PAH fluorescence and the LII overlap spectrally [52-56]. Moreover, the UV excitation used for the PAH-PLIF can be absorbed by the soot particles [52-56]. To resolve this, the following twofold steps were taken. First, the laser excitation energy was controlled to a low fluence to avoid the incandescence of the soot particles [2,56]. As mentioned earlier, the UV laser fluence was kept at low level of 250 mJ/cm^2 in the present study. Second, the detection of the PAH fluorescence signal was accomplished by integrating the prompt fluorescence signal, in a short detection gatewidth of 30 ns, right after the absorption of the laser pulse [2,49,56]. Since the fluorescence signal is short lived compared to the LII signal, the shorter detection gatewidth avoids the noise due to the LII signal (if any). Furthermore, researchers have provided the spectral resolutions for the PAH molecules by grouping them according to the number of the aromatic rings. It has been shown that the signals of 2- and 3-aromatic ring PAHs (naphthalene, anthracene, and derivatives) attribute to a wavelength close to 330 nm [57-59]. Using several ethylene coflow flames with different partially-premixing levels, McEnally and Pfefferle [60] compared the PAH-PLIF signals for naphthalene (C_{10}H_8) with its concentrations measured using the photoionization/time-of-flight mass spectrometer (PTMS), and demonstrated that the PAH-PLIF signals provide qualitative measurements of the naphthalene concentrations. To detect 2- and 3-ring aromatics, a detector of 334 nm wavelength was used in the current study. In addition, the detection wavelength of 400 nm has been known to correspond to the 4-aromatic

ring(A₄) pyrene (C₁₆H₁₀) [61], and hence it was used to detect the 4-ring aromatics. The other two detection wavelengths of 450 nm and 492 nm qualitatively represent the larger ring PAH molecules [53,62]. These wavelengths have not been directly related to the PAH ring sizes, as for the longer detection wavelengths the spectral separation of the fluorescence signals from large PAHs becomes complex [53,57,62]. It was observed in [55,63-65] that the PAH fluorescence signal using the 500 nm detection was spatially closest to the LII signal. As such, in our study, a 492 nm detection wavelength represents large PAH molecules formed right before the soot particle formation, which will be demonstrated later.

3. Computational specifications

The present counterflow non-premixed flames were simulated using the OPPDIF module in CHEMKIN-PRO [66], which is based on the plug-flow formulation of Kee *et al.* [67]. This counterflow flame model includes the GAS-PHASE KINETICS subroutine library and TRANSPORT subroutine package. The OPPDIF simulations were performed by adopting the Primary Reference Fuels + PAH + Alcohols + Ethers mechanism (Version POLIMI_PRF_PAH_ALCOHOLS_ETHERS_HT_1412, December 2014) of the Chemical Reaction Engineering and Chemical Kinetics (CRECK) Modeling Group [68-71]. This mechanism was employed in the current study because it can predict the formation of soot precursors up to the four-ring aromatics for butane and butanol isomers. The mechanism includes 317 species and 12353 reactions, and is referred as the POLIMI mechanism hereafter. While a detailed soot modeling considering the soot particle inception, coagulation, and growth processes was not incorporated herein, the computed spatially-resolved profiles of those PAHs included in the POLIMI mechanism would still provide insight into the PAH/soot formation for the C₄ fuels investigated.

4. Results and discussions

4.1. LII and PAH-PLIF images

Figure 2 shows a false color representation, not drawn to the scale, of the LII and PAH-PLIF images detected for an *n*-butanol sooting flame. The fuel stream was *n*-butanol/N₂ mixture with the fuel mole fraction of $X_F = 0.29$, while the O₂/N₂ oxidizer stream was maintained at the oxygen mole fraction of $X_{O_2} = 0.90$. The PAH-PLIF images shown in Fig. 2 are for 334, 400, 450, and 492 nm detection wavelengths, representing the sequence of the PAH formation with different ring sizes. It is noted that the PAH-PLIF signals for the detection wavelengths actually overlap, which can be seen in the spatially-resolved profiles to be shown later. Such overlap of PAH-PLIF signals is not shown in Fig. 2 for clarity. Shown in the representative Fig. 2, the PAH-PLIF images are closer to the fuel nozzle than the LII image. In addition, as the detection wavelength of the PAH-PLIF measurement becomes longer, corresponding to the larger ring size aromatics, the PAH-PLIF images shift closer to the LII image.

Figure 2: Images of LII and PAH-PLIF detected in a counterflow non-premixed flame for *n*-butanol (representative figure illustrating the relative spatial locations of the images, not shown to the scale). Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

4.2. Calibration for *n*-butanol and *iso*-butane flames

In Figs. 3(a) and 3(b), the spatial distribution profiles of soot volume fraction measured using the LII and LE techniques, as described in [49], are shown for *n*-butanol sooting flame of Fig. 2 at seven axial locations (z) from the bottom fuel nozzle. With increasing z , Figs. 3(a) and 3(b) show the results in the soot growth and soot decomposition regimes, respectively. At the ‘Calibration Point’ for $z=4.84$ mm indicated in Fig. 3(a), the LII signal was compared with the quantitative measurement of soot volume fraction using the LE technique. The refractive index used in this study is $m = 1.57 - 0.56i$, which is a widely used value and has been validated against a wide range of fuels and flame environments, as discussed in [49]. A calibration factor of 3.11×10^8 was then calculated with this comparison, which was found to be very similar to the calibration factor of 3.05×10^8 determined with a sooting ethylene flame in our previous study [49]. Figures 3(c) and 3(d) further show the similar results of the *iso*-butane sooting flame with $X_F = 0.29$ and $X_{O_2} = 0.90$. The calibration factor was determined to be 3.08×10^8 , which, again, is very close to those of ethylene and *n*-butanol. This finding, therefore, suggests that for the conditions investigated herein, the variation in the soot optical properties is insignificant for the oxygenated fuels like *n*-butanol and the non-oxygenates like ethylene and *iso*-butane.

Using these calibration factors determined at the corresponding ‘Calibration Point’, the quantitative values for the LII signals at different radial-axial locations (r, z) were then calculated. As shown in Fig. 3, the radial soot volume fraction distributions determined from both the LII and LE techniques compare very well for the other axial locations. Moreover, the LE- and LII-measured soot volume fraction profiles are shown to be radially symmetrical, which further demonstrates the stability of the sooting flames for liquid butanols established in the current counterflow burner facility.

Figure 3: Comparison of soot volume fraction distributions in counterflow non-remixed flames measured using LE and LII: (a) soot formation zone for *n*-butanol, (b) soot decomposition and oxidation zone for *n*-butanol, (c) soot formation zone for *iso*-butane, and (d) soot decomposition and oxidation zone for *iso*-butane, where z represents the distance from the fuel nozzle. Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$. Solid symbols/black lines are for LE measurements and hollow symbols/gray lines are for LII measurements.

4.3. Test matrix

Table 2 lists the calculated adiabatic flame temperatures (T_{ad}) for all the fuels investigated using the thermodynamic database of the POLIMI mechanism [68–71]. In addition, the maximum flame temperatures (T_{max}) obtained from the counterflow flame simulations are listed in Table 2. While the reaction kinetics of the fuel pyrolysis and oxidation, the aromatic formation, the PAH mass growth and oxidation, and the soot chemistry are temperature sensitive, for a given set of X_F and X_{O_2} , the slight differences in T_{ad} and T_{max} , within the isomers and between butanes and butanols, are not expected to have a major impact on the PAH and soot formation processes in

different fuels. Furthermore, the locations of T_{max} for these fuels under the same flow conditions are approximately the same, as can be seen from the spatially-resolved temperature profiles shown in the next section.

Table 2 Calculated adiabatic flame temperatures (T_{ad}), maximum flame temperatures (T_{max}) in the given counterflow conditions, and stoichiometric mixture fractions (Z_{st}) for butane and butanol isomers.

Fuel	Fuel Stream		Oxidizer Stream		Adiabatic Flame Temperature T_{ad} (K)	Maximum Flame Temperature T_{max} (K)	Stoichiometric Mixture Fraction Z_{st}
	X_F	X_{N_2}	X_{O_2}	X_{N_2}			
<i>n</i> -Butane	0.29	0.71	0.90	0.10	2991	2872	0.357
<i>iso</i> -Butane	0.29	0.71	0.90	0.10	2988	2868	0.357
<i>n</i> -Butanol	0.29	0.71	0.90	0.10	2946	2829	0.404
<i>iso</i> -Butanol	0.29	0.71	0.90	0.10	2943	2825	0.404
<i>sec</i> -Butanol	0.29	0.71	0.90	0.10	2940	2821	0.404
<i>tert</i> -Butanol	0.29	0.71	0.90	0.10	2934	2813	0.404

In addition, the values of stoichiometric mixture fraction, Z_{st} , defined as:

$$Z_{st} = \left(\frac{X_{O_2}}{W_L \nu_{O_2}} \right) / \left(\frac{X_{O_2}}{W_L \nu_{O_2}} + \frac{X_F}{W_0 \nu_F} \right), \quad (1)$$

for different mixture conditions are also listed in Table 2. In Eq. (1), ν_{O_2} and ν_F are the stoichiometric coefficients of O_2 and fuel, respectively, and W_L and W_0 are the average molecular weights of the mixtures at the oxidizer ($z=L$) and the fuel ($z=0$) stream boundaries, respectively. In combustion theory, the mixture fraction is a normalized coupling function with the mixture fraction values of 0 and 1 defining the oxidizer and fuel stream boundaries, respectively [72]. In the flame sheet limit, combustion is considered to be stoichiometrically concentrated and completed at the mixture fraction value of Z_{st} . For all the mixture compositions investigated herein, $Z_{st} < 0.5$, as shown in Table 2, and hence the “flame sheets” are all situated on the oxidizer side of the stagnation plane. Although Z_{st} has been shown to have a significant effect on soot formation, for a given set of X_F and X_{O_2} the differences in Z_{st} due to the small

differences in molecular weights and stoichiometric coefficients for butanes and butanols are deemed insignificant. Therefore, the effect of Z_{st} in comparing the sooting propensity among different fuels is not considered in the present study.

Since soot formation is a rate-limiting process, it depends on the strain rate that characterizes the residence time experienced by the reactants in the combustion zone of a counterflow non-premixed flame. A higher strain rate implies a shorter residence time experienced by the reactant mixture. In this study, as the nozzle-generated exit flow is plug-like, the global strain rate (K), based on the relation of Seshadri and Williams [73]:

$$K = \frac{2V_L}{L} \left(1 + \frac{V_0 \sqrt{\rho_0}}{V_L \sqrt{\rho_L}} \right), \quad (2)$$

is used to represent the strain rate effect. In Eq. (2), V is the bulk velocity at the nozzle exit, ρ is the mixture density, and the subscripts 0 and L represent the fuel ($z=0$) and oxidizer ($z=L$) boundaries, respectively. Equation (2) also takes the effects of varying densities at two boundaries into account. For the bulk velocities of $V_0 = V_L = 14.9 \text{ cm/s}$ used in all of the present experiments, the global strain rate is $K=57 \text{ s}^{-1}$.

4.4. LII and PAH-PLIF results

The fuel molecular structure plays an important role in the PAH formation and growth processes as it can lead to different concentrations of precursors which can activate PAH-related reactions. Regarding the role of acetylene (C_2H_2), as it maintains relatively high concentration in the high-temperature region, PAHs can be produced through the sequential pathways of H-abstraction-acetylene-addition (HACA) reactions. Since the soot models based on the HACA mechanism underestimate the PAH and soot formations [10-15], additional reactions, including the reasonably stable aromatic radicals formed through the odd-carbon-atom pathways have been

suggested to enhance the PAH formation reactions. Hence, the propargyl (C_3H_3) recombination reaction is currently considered as one of the important reactions in the incipient ring formation process. Moreover, these odd-carbon-atom pathways are also considered important in PAH growth mechanisms [26-32]. In the PAH formation process, a competition between these reaction pathways is present, based on the amounts of the precursors (e.g., C_2H_2 and C_3H_3) available locally and the flame conditions favoring these reactions [26].

Figure 4 shows the axial profiles of relative LII and PAH-PLIF signals along the centerline of the counterflow flames of butane and butanol isomers. Again, the experimental conditions for these flames were $X_F=0.29$, $X_{O_2}=0.90$, and $K=57\text{ s}^{-1}$. The PAH-PLIF signal profiles for the detection wavelengths of 334 nm, 400 nm, 450 nm, and 492 nm shown were scaled by the maximum PAH-PLIF signal for the *n*-butane flame at 492 nm detection wavelength, which is the largest PAH signal across all the flames studied in Fig. 4. It is noted that considering the temperature sensitivity and concentration dependence of the PAH-PLIF signals from the aromatics of different ring sizes formed at different axial locations, the direct comparison of PAH-PLIF signals between two different detection wavelengths should be taken with caution. On the other hand, the LII profile for each flame was normalized with the corresponding maximum LII signal in order to demonstrate the relative spatial locations of the PAH-PLIF profiles for different detection wavelengths (hence different aromatic ring sizes). As demonstrated in Fig. 4, with the same values of X_F , X_{O_2} , and K for all counterflow non-premixed flames, the spatial locations of the PAH-PLIF profiles across the C_4 fuels are almost the same for a given detection wavelength. Using the POLIMI mechanism, the computed spatially-resolved profiles, including temperature and the mole fractions of acetylene, propargyl, and benzene, have also been shown in Fig. 4 for the comparison. As mentioned earlier, the locations of T_{max} are

Figure 4: Spatial profiles of relative LII and PAH-PLIF (detection wavelengths of 334 nm, 400 nm, 450 nm, and 492 nm) signals along the centerline, as well as the computed profiles of temperature and mole fractions of acetylene, propargyl, and benzene, for: (a) *n*-butane, (b) *iso*-butane, (c) *n*-butanol, (d) *iso*-butanol, (e) *sec*-butanol, and (f) *tert*-butanol flames. Conditions: $X_F = 0.29$, $X_{O_2} = 0.90$, and $K = 57 \text{ s}^{-1}$.

almost the same, situated at 5.25 mm distance from the fuel nozzle. In this study, the detection wavelength of 334 nm represents the PAH-PLIF measurements at the inception stage, as it characterizes the PAHs with 2 and 3 aromatic rings. It is of interest to note that the computed mole fraction profiles of benzene for all flames investigated peak before (i.e. closer to the fuel nozzle) the corresponding maximum signal for the 334 nm detection.

It can also be observed from Fig. 4 that for all the butane and butanol isomers the PAH profiles are closer to the fuel side than the LII profile, indicating that PAHs grow from the fuel side. The results for all the flames also show that with the increase in detection wavelength the PAH-PLIF profiles move closer to the LII profile. This shift in PAH-PLIF profiles with increasing detection wavelength in turns indicates that the longer (shorter) detection wavelength corresponds to the larger (smaller) aromatic ring size of PAH's. A comparison of the PAH-PLIF profiles in Fig. 4 across the flames for any of the detection wavelengths shows that while their profile shapes appear similar, the maximum relative signal values vary. Such behavior can be associated with the fuel structural differences. This is further analyzed in details in the following.

In general, the hydrocarbons are known to decompose by either the unimolecular dissociation or bimolecular H-abstraction. The dissociation process is also known to occur by the complex fission or simple fission. It is theorized that the butanol isomers are able to produce H_2O through the process of complex fission [74-79]. Since the dominant pathways of initial fuel breaking depend on the structure of the fuel, understanding the initial fuel breaking pathways is important to understand the formation of the first aromatic rings [80]. In order to aid the interpretation of the present experimental results, the fuel decomposition pathways for the butanol isomers are described hereafter. The complex fission process takes place by bonding between the hydrogen (H) and hydroxyl (OH) to form H_2O , and the α and β carbon atoms form a double bond between

them to form butene [76]. In the simple fission process, first a methyl radical is abstracted from the α carbon atom, and then hydrogen radical is abstracted from the oxygen atom to form a double bond between the α carbon atom and oxygen atom to form acetone [77,78]. In the process of H-atom abstraction, first a hydrogen atom is abstracted from the β carbon atom, then a hydroxyl radical is abstracted from the α carbon atom, thereby facilitating the formation of a double bond between the α and β carbon atoms to form butene [75-77]. The step of the complex fission process depends on the structure of the fuel and this determines the amount of butene produced by each of the butanol isomers. Structurally, in the *tert*-butanol isomer, the hydroxyl group has a maximum number (9) of neighboring hydrogen atoms available to form the complex bonds, and hence this helps in unimolecular elimination of water. This step has been reported as the dominant pathway in butene formation [81-84]. Similar complex fission reaction pathways are possible for the *n*-butanol, *iso*-butanol, and *sec*-butanol isomers, as for these fuels, the hydroxyl group has 2, 1, and 5 neighboring hydrogen atoms to form the complex bond to eliminate water [84]. For these three isomers, other competing fuel destruction pathways of H-abstraction, followed by the β -scission of the C-O bond have also been known [81,82]. The measurements of the butene for these butanol isomers, using the Electron Ionization-Molecular Beam Mass Spectrometry (EI-MBMS) technique, by Oßwald *et al.* [85] in a flat stabilized flames on McKenna burner, showed that the *tert*-butanol isomer produces the maximum amount of the butene, followed by *iso*-butanol, *sec*-butanol, and *n*-butanol in the decreasing order. The importance of the butene formation is related to the propargyl and first aromatic benzene ring formation [82,85]. In addition, Oßwald *et al.* [85] have experimentally shown that the propargyl radical formation follows the order of butene formation. The reactions of allene and allyl production from butene have been envisaged as the responsible reactions, linking the butene and

the propargyl [86,87]. Further, the experimental measurements, by Oßwald *et al.* [85] using the Particle-Ionization-Molecular-Beam-Mass-Spectrometry (PI-MBMS), and by McEnelly and Pfefferle [82] using the mass spectroscopy technique, have shown that the first benzene ring formation follows the order of propargyl formation, and at the initial aromatic ring formation stage the propargyl recombination reaction is the most important. Similar observations linking the propargyl with benzene formation have been made by Hansen *et al.* [88] and Miller *et al.* [89]. From these theoretical and experimental backgrounds, it is established that the initial aromatic ring formation for butanols is governed by the propargyl radical.

The soot formation process can be divided into the inception and growth stages. Camacho *et al.* [90] and McEnelly and Pfefferle [82] have noted that a direct link between the fuel structure and the PAHs at the inception stage can be established. Firstly, the PAH-PLIF profiles measured at 334 nm detection wavelength for different flames shown in Fig. 4 are analyzed and compared. As stated earlier, this detection wavelength corresponds to PAHs with 2 and 3 aromatic rings, and hence this detection wavelength represents the PAHs at the inception stage. Figure 5(a) shows and compares the maximum relative PAH-PLIF signals at 334 nm detection wavelength for butane and butanol isomers. It is seen that in terms of the amounts of 2- and 3-ring aromatics produced by these fuels, they are ordered as *tert*-butanol > *iso*-butane > *iso*-butanol > *sec*-butanol > *n*-butane > *n*-butanol. Similar rankings have been observed by McEnelly and Pfefferle [82] in their benzene measurements. It is also noted from Fig. 5(a) that the PAH-PLIF signal at 334 nm for *iso*-butane is larger than that for *n*-butane. Similar PAH inception ranking for the butane isomers was also observed by Camacho *et al.* [90], and McEnelly and Pfefferle [82], as they noted that the branched chain isomers produce more propargyl than the straight chain isomers. Additionally, the straight chain isomer was found to produce more acetylene than the branched

chain isomer [82]. These literature results indicate that at the inception stage the odd-carbon-atom pathway of propargyl recombination dominates. By similar analogy, the results which have been shown in Fig. 5(a) for the butanol isomers can be explained and inferred, as the most branched isomer, *tert*-butanol, has the maximum PAH-PLIF signal, followed by *iso*-, *sec*-, and *n*-butanol, in the order of the degree of branching of these isomers as defined in [82].

Figure 5: Comparison of maximum relative PAH-PLIF signals measured for butane and butanol isomers: (a) detection wavelength of 334 nm corresponding to 2- and 3-ring aromatics and (b) detection wavelength of 400 nm corresponding to 4-ring aromatics. Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

Based on the results in Fig. 4, Fig. 5(b) compares the maximum relative PAH-PLIF signals at the detection wavelength of 400 nm for different flames. As discussed earlier, this detection wavelength corresponds to pyrene. For this detection wavelength, the isomers studied are ranked as *tert*-butanol > *iso*-butane > *iso*-butanol > *sec*-butanol > *n*-butane > *n*-butanol. This ranking follows that observed for the 2- and 3-ring aromatics produced. As the present ranking is consistent with the literature results discussed earlier, it can be inferred that even up to the 4-ring aromatics formation, the odd-carbon-atom pathways of PAH formation dominate. The dominance of the odd-carbon-atom pathways via propargyl is further demonstrated in Sec. 4.6 and explained through the path analyses discussed in Sec. 4.7.

From our previous study of the soot formation process of the counterflow non-premixed flames [49], the sooting tendencies for these fuels were ranked as *n*-butane > *iso*-butane > *tert*-butanol > *n*-butanol > *iso*-butanol > *sec*-butanol. Shown in Fig. 6 are these rankings for the flames of Fig. 4 by plotting their maximum soot volume fractions. In Fig. 6(a) the maximum soot volume fraction values with y-axis scale of $10^{-5} - 10^{-4}$, while in Fig. 6(b) these are shown using a y-axis scale of $10^{-6} - 10^{-5}$ so that the rankings for the butanol isomers can be prominently seen. In our previous study [49], it was also observed that the sooting propensity rankings in terms of soot volume fraction remained the same as shown in Fig. 6 for varying fuel mole fractions, oxidizer mole fractions, and strain rates. Comparing these with the current PAH-PLIF measurements at the inception stage shown in Fig. 5, it can be concluded that the PAH formation at the inception stage does not correlate with the amount of soot formed. As discussed earlier, the PAH growth and the soot formation processes involve various complex parallel pathways, and hence a direct correlation between the soot volume fraction and the PAH formation at the inception stage may not exist.

For further analysis, the maximum relative PAH-PLIF signals for all the detected wavelengths are compared in Fig. 7 for the straight- and branched-chain isomers. The error bars in Fig. 7 are based on twice the standard deviation of the repeated measurements. A comparison of *n*-butane and *iso*-butane is shown in Fig. 7(a), and it is seen that *iso*-butane has a larger signal than *n*-butane for the 334 nm detection wavelength, which could be due to the dominance of the odd-carbon-atom pathways discussed in [82]. The same trend continues for the detection wavelengths of 400 and 450 nm, as shown in Fig. 7(a), consistent with the findings of [82] for *iso*-butane that the odd-carbon-atom pathways remain dominant at this stage. However, a comparison of PAH-PLIF signals at the detection wavelength of 492 nm shows that *n*-butane

turns out to have larger signal than *iso*-butane. Since the location of the peak PAH-PLIF signal at 492 nm detection wavelength is closer to the sooting flame, the larger signal for *n*-butane could be because the temperature-sensitive HACA reactions for *n*-butane enhance the PAH formation at this growth stage as discussed in [82].

Figure 6: Comparison of peak soot volume fractions: (a) all the butane and butanol isomers and (b) butanol isomers. Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

In Fig. 7(b), a comparison for *n*-butanol and *iso*-butanol has been presented. While *iso*-butanol shows larger PAH-PLIF signal than *n*-butanol for the detection wavelengths of 334 and 400 nm, *n*-butanol exhibits larger PAH-PLIF signal for the detection wavelengths of 450 and 492 nm. Since the results are consistent with those of [82], it is inferred that the consequence of the branched chain isomer producing more propargyl and its effect at the PAH inception stage [82] result in larger PAH-PLIF signal for *iso*-butanol up to the detection wavelength of 400 nm. However, from 450 nm onwards the PAH-PLIF signal for *n*-butanol being larger suggests that the HACA mechanism for *n*-butanol propels the growth of PAHs (larger aromatic ring size) in comparison to *iso*-butanol [82]. Similar findings were observed when comparing *sec*-butanol and *n*-butanol, as shown in Fig. 7(c).

Figure 7: Comparison of maximum relative PAH-PLIF signals for 334 nm, 400 nm, 450 nm, and 492 nm detection wavelengths: (a) n -butane and iso -butane, (b) n -butanol and iso -butanol, (c) n -butanol and sec -butanol, and (d) n -butanol and $tert$ -butanol. Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$. Lines are connected to guide the discernment.

Further, in Fig. 7(d), a comparison of n -butanol and $tert$ -butanol is shown. Consistent with the demonstration in [82] that the odd-carbon-atom pathways for the branched chain isomer dominate, $tert$ -butanol is seen to have larger PAH-PLIF signal than n -butanol at 334 nm detection wavelength. This behavior continues for the other detection wavelengths of 400, 450, and 492 nm. Following the literature results, this suggests that for $tert$ -butanol, the odd-carbon-atom pathways produce an abundance of incipient aromatics, such that the odd-carbon-atom pathways of the PAH growth remain a dominant pathway. Other than $tert$ -butanol, when n -butanol was compared with the other two isomers, the HACA mechanism for n -butanol is expected to account for the formation of larger PAHs.

Figures 8(a) and 8(b) compare the maximum relative PAH-PLIF signals for all C₄ flames measured at the detection wavelengths of 450 nm and 492 nm, respectively. Since these two detection wavelengths characterize PAHs larger than 4 aromatic rings, as discussed earlier, Fig. 8 demonstrates the rankings for the PAH growth stage. The ranking for 450 nm detection shows *iso*-butane > *n*-butane > *tert*-butanol > *n*-butanol > *iso*-butanol > *sec*-butanol. At the detection wavelength of 492 nm, signifying much larger PAHs, the ranking becomes *n*-butane > *iso*-butane > *tert*-butanol > *n*-butanol > *iso*-butanol > *sec*-butanol. The rankings, as shown in Fig. 8 for the PAH growth stage, are seen to be different from those shown in Fig. 5 for the PAH inception stage. As the 492 nm detection wavelength represents large PAHs formed prior to the formation of soot particles, the PAH formation ranking in Fig. 8(b) is seen to be consistent with the sooting tendency ranking displayed in Fig. 6 and that reported in [49].

Figure 8: Comparison of maximum relative PAH-PLIF signals measured for butane and butanol isomers: (a) large aromatics measured with detection wavelength of 450 nm and (b) large aromatics measured with detection wavelength of 492 nm. Conditions: $X_F = 0.29$, $X_{O_2} = 0.90$, and $K = 57 \text{ s}^{-1}$.

4.5. Non-premixed counterflow flame simulations

From the experimental results at the inception stage and based on their consistency with the literature studies, it is inferred that the amount of the PAH formed by these isomers is expected to show a correlation with the ability of each fuel to produce the propargyl. To correlate the incipient PAH formation and the precursors such as the acetylene and the propargyl, the experimental conditions were simulated using the POLIMI mechanism [68-71]. Since the present experimental results only provide qualitative measurements, a quantitative comparison with the simulated results is not made. Hence, these experimental and simulated results are compared in terms of predictability of the rankings. The calculated peak mole fractions of the acetylene and the propargyl formed in the flames by these isomers are shown in Figs. 9(a) and 9(b), respectively. In terms of the peak acetylene formation, the isomers are ranked as *n*-butane > *iso*-butane > *n*-butanol > *sec*-butanol > *iso*-butanol > *tert*-butanol. As discussed in McEnally and Pfefferle [82], the straight chain isomers produce more acetylene than the branched chain isomers. The comparison of these isomers in terms of the peak propargyl formation shows that the ranking is *tert*-butanol > *iso*-butane > *iso*-butanol > *sec*-butanol > *n*-butane > *n*-butanol. This propargyl ranking is consistent with the experimental ranking for the incipient PAHs shown in Fig. 5. Further, the A₁-ring (benzene, C₆H₆) in Fig. 9(c), the A₂–A₃-ring PAHs (naphthalene, C₁₀H₈; anthracene, C₁₄H₁₀) in Fig. 9(d), and the A₄-ring PAH (pyrene, C₁₆H₁₀) in Fig. 9(e) show the same ranking as the propargyl in Fig. 9(b). From the past studies [20,25,82], it has been shown that in the formation of benzene ring the propargyl radical plays an important role. Therefore, the ranking of A₁-ring formation (benzene, C₆H₆) in Fig. 9(c) follows the trend for propargyl radical formation in Fig. 9(b).

Figure 9: Comparison of calculated peak mole fractions using the POLIMI mechanism [68-71] for butane and butanol isomer: (a) acetylene (C_2H_2), (b) propargyl (C_3H_3), (c) A_1 aromatics (C_6H_6), (d) A_2 and A_3 aromatics ($C_{10}H_8$ and $C_{14}H_{10}$), and (e) A_4 aromatics ($C_{16}H_{10}$). Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

From the experimental results shown in Fig. 5, the A_2 – A_3 and the A_4 rankings show the same trend as the simulated results shown in Figs. 9(d) and 9(e). It will be demonstrated in due course that the simulated results exhibit the importance of the odd-carbon-atom pathways through the propargyl recombination at the incipient stage. Since the POLIMI mechanism [68-71] does not

consider the PAHs larger than A₄, the experimental results based on the 450 nm and 492 nm detection wavelengths shown in Fig. 8 cannot be simulated and compared.

4.6. Effects of fuel blending

With the discussion and comparison with the literature studies so far, it can be inferred that the PAH formation at the inception stage is mostly governed by the ability of the isomers to produce the propargyl and hence by the odd-carbon-atom pathway of the initial aromatic ring formation. At the PAH growth stage, however, the HACA mechanism is also expected to play a role, as seen in the sooting tendency for some of the fuels. To further investigate the role of the HACA mechanism, the two straight chain fuels, *n*-butane and *n*-butanol, were blended with their respective branched chain isomers. The total fuel mole fraction was still kept constant at $X_F=0.29$, while the blending percentage (β) is defined as:

$$\beta = \frac{X_{F,branched}}{X_F} \times 100, \quad (3)$$

where $X_{F,branched}$ is the mole fraction of the branched chain isomer in the fuel stream. As the fuels from the same isomeric class with the same molecular weight were blended, for the same oxidizer stream, the Z_{st} values for binary blend/N₂ mixtures remain the same as those of the respective neat components listed in Table 2, when the total fuel mole fraction is fixed at $X_F=0.29$. In addition, because of the small difference in T_{ad} or T_{max} for the isomers of the same class, as shown in Table 2, the variation of T_{ad} or T_{max} with β is considered insignificant. Hence, any change in PAH-PLIF signals with varying fuel blending ratios observed in the current experiments can be attributed to the fuel structure effects.

With $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$, the relative intensities of the PAH-PLIF signals for the binary blends of *n*-butane/*iso*-butane and *n*-butanol with other butanol isomers varying from

$\beta=0\%$ to 100% were measured. Figure 10 shows such experimental results in order to identify the synergistic effects. Again, the PAH-PLIF signals were scaled by the maximum value for the detection wavelength of 492 nm for the n -butane flame. Two different fuel blending effects were generally observed in Fig. 10. First, an increase in the PAH-PLIF signal followed by a decrease, with the increase in β , was seen. For brevity, this behavior in the PAH-PLIF signal is named as ‘positive synergy’ in the current study. The second type of the blending effect was opposite to the first one, which exhibits a decrease in the PAH-PLIF signal followed by an increase, with the increase in β . This behavior in the PAH-PLIF signal is named as ‘negative synergy’ herein.

Figure 10: Variations of maximum relative PAH-PLIF signals for 334 nm , 400 nm , 450 nm , and 492 nm detection wavelengths with blending percentage: (a) blending *iso*-butane in *n*-butane, (b) blending *iso*-butanol in *n*-butanol, (c) blending *sec*-butanol in *n*-butanol, and (d) blending *tert*-butanol in *n*-butanol. Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57\text{ s}^{-1}$. Lines are connected to guide the discernment.

These behaviors, as shown in Fig. 10, can be examined by comparing them with the simulated results of the acetylene and the propargyl. In Figs. 9 and 11-14, the simulated results of the peak mole fractions of the acetylene and the propargyl using the POLIMI mechanism for the individual fuels and the binary blends are shown, along with those of the A_1 – A_4 aromatics. The detailed discussions on Figs. 11-14 will be provided later. As observed from Fig. 9, the straight chain isomers produce more acetylene than the branched chain isomers, while the branched chain isomers produce more propargyl than the straight chain isomers. From Figs. 11-14, a uniform observation of an increase in the propargyl concentration and a decrease in the acetylene concentration with increasing β can be made. Considering these, ‘positive synergy’ is explained in the following.

Figure 11: Variations of calculated peak mole fractions using the POLIMI mechanism [68-71] with blending percentage for blending *iso*-butane in *n*-butane: (a) propargyl (C_3H_3), (b) A_1 aromatics (C_6H_6), (c) A_2 , A_3 , and A_4 aromatics ($C_{10}H_8$, $C_{14}H_{10}$, and $C_{16}H_{10}$, respectively), and (d) acetylene (C_2H_2). Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

Figure 12: Variations of calculated peak mole fractions using the POLIMI mechanism [68-71] with blending percentage for blending *iso*-butanol in *n*-butanol: (a) propargyl (C_3H_3), (b) A₁ aromatics (C_6H_6), (c) A₂, A₃, and A₄ aromatics ($C_{10}H_8$, $C_{14}H_{10}$, and $C_{16}H_{10}$, respectively), and (d) acetylene (C_2H_2). Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

For the detection wavelength of 334 nm, as shown in Fig. 7(a), the PAH-PLIF signal for *iso*-butane is larger than that for *n*-butane. As previously discussed, this can be inferred to be the dominant role of the odd-carbon-atom pathways involving the propargyl in the PAH inception stage for *iso*-butane. It is seen from Fig. 10(a) that the relative PAH-PLIF signal for the detection wavelength of 334 nm increases from $\beta=0\%$ (pure *n*-butane) to $\beta=70\%$, followed by a decrease when further increasing *iso*-butane blending to $\beta=100\%$ (pure *iso*-butane). In view of the consistent increase in the propargyl concentration in Fig. 11(a) with increasing β , this non-monotonic behavior in the PAH-PLIF signal for the 334 nm detection wavelength can be argued to be related to the other parallel reactions competing with the odd-carbon-atom pathways, such as the HACA mechanism. An initial increase in *iso*-butane blending provides more aromatic

rings, and hence in conjunction with the HACA mechanism, this results in the ‘positive synergy’, as the increase in the PAH-PLIF signals for these binary blends surpass those of pure *n*-butane and pure *iso*-butane. However, the decrease in acetylene concentration with increasing *iso*-butane blending, as shown in Fig. 11(d), could lead to a decrease in the PAH-PLIF signal with the detection wavelength of 334 nm for $\beta=80\text{--}100\%$.

Figure 13: Variations of calculated peak mole fractions using the POLIMI mechanism [68–71] with blending percentage for blending *sec*-butanol in *n*-butanol: (a) propargyl (C_3H_3), (b) A₁ aromatics (C_6H_6), (c) A₂, A₃, and A₄ aromatics ($C_{10}H_8$, $C_{14}H_{10}$, and $C_{16}H_{10}$, respectively), and (d) acetylene (C_2H_2). Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

On the other hand, the ‘negative synergy’ exhibits opposite effects with increasing β . As seen from Fig. 7(a), *n*-butane has a larger PAH-PLIF signal for the 492 nm detection wavelength than *iso*-butane. Based on this experimental finding and the simulated results, the importance of the acetylene in the large PAH formation through the HACA mechanism is suggested. In addition, it is observed from Fig. 10(a) for the detection wavelength of 492 nm that the relative

PAH-PLIF signal decreases from $\beta=0\%$ (pure *n*-butane) to $\beta=50\%$, and then increases with increasing *iso*-butane blending towards $\beta=100\%$ (pure *iso*-butane). Again, a monotonic decrease in acetylene concentration with increasing β can be seen from Fig. 11(d). This decrease in acetylene concentration in turns impedes the PAH formation mostly dominant through the HACA pathways along with the odd-carbon-atom pathways. Since the propargyl concentration increases with increasing β , as shown in Fig. 11(a), a further increase in *iso*-butane blending for $\beta=50\text{--}100\%$ adds the aromatic rings through the odd-carbon-atom pathways, thereby providing more sites for PAH growth and leading to an increase in the PAH-PLIF signal for the 492 nm detection wavelength. These synergistic results further indicate that both the propargyl and the acetylene are involved in the PAH formation, and the concentrations of these precursors, as well as the local flame environment/condition, determine the dominant role played by either of these in the PAH formation.

Based on the above discussions, the experimental results of Fig. 10 can then be better understood and explained. In Fig. 10(a), the changes in the relative PAH-PLIF signal intensities as a result of blending *iso*-butane in *n*-butane have been shown. For the detection wavelengths of 334, 400, and 450 nm, the PAH-PLIF signals exhibit ‘positive synergy’, which can be inferred by the dominance of the odd-carbon-atom pathways at this inception stage for *iso*-butane. At the detection wavelength of 492 nm, the ‘negative synergy’ was observed, which emphasizes the importance of the HACA mechanism for *n*-butane at this growth stage.

Figure 10(b) shows the experimental results of blending *iso*-butanol in *n*-butanol. Similar to the binary blends of *iso*-butane and *n*-butane, synergistic effects have been observed. For the detection wavelengths of 334 and 400 nm, the ‘positive synergy’ can be observed, suggesting that for these wavelengths of detection the odd-carbon-atom pathways for *iso*-butanol produce

relatively more PAHs than *n*-butanol. For the detection wavelengths of 450 and 492 nm, the ‘negative synergy’ can be observed, thereby implying the importance of the HACA mechanism enhancing the PAH growth for the *n*-butanol at this stage. The same observations have been made for the blending effects of *sec*-butanol and *n*-butanol as shown in Fig. 10(c). In Fig. 10(d), when blending *tert*-butanol in *n*-butanol, all the detection wavelengths show the ‘positive synergistic’ effect. This further emphasizes the importance of the odd-carbon-atom pathways in the PAH formation for *tert*-butanol.

Figure 14: Variations of calculated peak mole fractions using the POLIMI mechanism [68-71] with blending percentage for blending *tert*-butanol in *n*-butanol: (a) propargyl (C_3H_3), (b) A_1 aromatics (C_6H_6), (c) A_2 , A_3 , and A_4 aromatics ($C_{10}H_8$, $C_{14}H_{10}$, and $C_{16}H_{10}$, respectively), and (d) acetylene (C_2H_2). Conditions: $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

The binary fuel blend experiments of Fig. 10 are also simulated using the POLIMI mechanism [68-71]. For the binary blends of *n*-butane and *iso*-butane, Fig. 11 demonstrates that the peak mole fractions of the propargyl and the A_1 – A_4 ring PAHs increase with increasing β ,

while the peak mole fraction of the acetylene decreases. Although a non-monotonic response ('positive or negative synergy') was observed in the PAH-PLIF experiments shown in Fig. 10(a), such a behavior is not observed in the simulations. Similar observations are made for blending the branched chain butanols in *n*-butanol, as shown in the simulated results of Figs. 12–14, namely a monotonic increase in the amounts of the propargyl and the A₁–A₄ ring PAHs formed, and a monotonic decrease in the amount of the acetylene formed. This discrepancy in the experimental and simulated results is further investigated by conducting path analyses of PAH formation in the POLIMI mechanism [68-71], as well as by examining the role of the acetylene in PAH formation along with the dominance of the propargyl at the inception stage.

4.7. PAH formation pathways

In the present path analyses, the *n*-butane flame with $X_F=0.29$, $X_{O_2}=0.90$, and $K=57\text{ s}^{-1}$ was used as a representative condition for the demonstration. For each of the aromatic species of interest, the spatially-integrated rates of the production for the contributing reaction pathways were taken from the simulation. The percentage contribution from each reaction pathway was calculated relative to the sum of all the related, spatially-integrated rates of production. Figures 15(a) and 15(b) demonstrate the major kinetic pathways leading to the formation of the benzene (C₆H₆) and the phenyl (C₆H₅), respectively. It can be seen from Fig. 15(a) that 56.5% of the benzene formation is due to the conversion of the phenyl by reacting with the hydrogen radical. Such conversion of phenyl, reacting with PC₃H₄, C₃H₆, C₂H₄, and CH₃, totals to 9.20%, while the similar conversion by reacting with C₂H₂ accounts for 1.5% of the benzene formation. Moreover, the propargyl recombination reaction, $C_3H_3+C_3H_3(+M)\rightarrow C_6H_6$, and the acetylene pathway, $C_2H_2+C_4H_4\rightarrow C_6H_6$, contribute 24.42% and 0.26%, respectively. The reaction pathway from methylcyclopentadiene also shows a 2.9% contribution. It has to be pointed out that the fulvene chemistry is not considered in the POLIMI mechanism, and hence is not shown here.

Figure 15: Kinetic pathways of formation of (a) A_1 aromatics (benzene, C_6H_6) and (b) A_1 aromatic radicals (phenyl, C_6H_5), showing percentage contributions through various reactions based on the POLIMI mechanism [68-71]. Conditions: n -butane, $X_F=0.29$, $X_{O_2}=0.90$, and $K=57 \text{ s}^{-1}$.

At first glance Fig. 15(a) seems to suggest that the main formation of the benzene is from the phenyl at 56.5%. However, it can be seen from Fig. 15(b) that there are reaction channels, converting the phenyl back to the benzene, in a significant portion. In particular, in the phenyl formation pathways shown in Fig. 15(b), the conversion from benzene by reacting with H and

CH₃ contribute 81.95% and 5.71%, respectively. As the precursor species, including propargyl, acetylene, etc., are the fundamental building blocks in the aromatic formation process [24], they are expected to make major contributions. Therefore, apart from the inter-conversion reactions, the most important pathway of benzene formation is from propargyl. Similarly, in the phenyl formation, Fig. 15(b) shows that $C_3H_3 + C_3H_3 \rightarrow C_6H_5 + H$ and $C_4H_3 + C_2H_2 \rightarrow C_6H_5$ contribute 5.71% and 0.33%, respectively, with the propargyl pathway being more significant. These results indicate that for the first aromatic ring formation process in the POLIMI mechanism, the propargyl pathways are dominant as compared to the acetylene pathways.

The simulated results shown in Figs. 16–18 further illustrate that the major pathways in the POLIMI mechanism for the PAH growth to the 2-, 3-, and 4-ring aromatics, are through the odd-carbon-atom pathways, as indicated by the solid arrows for the first level pathways and the dashed arrows for the second level pathways. It is noted that the species in the second level originate mostly from the odd-carbon-atom pathways, which are described in details in the following discussion.

It is seen from Fig. 16(a) that for the A₂ ring, naphthalene (C₁₀H₈), the major formation pathways, apart from the stabilizing inter-conversion reactions, are through the methylnaphthalene pathway, $C_{10}H_7CH_3 + H \rightarrow C_{10}H_8 + CH_3$, and the methylnaphthalene radical pathway, $C_{10}H_7CH_2 + CH_3 \rightarrow C_{10}H_8 + C_2H_4$, contributing 14.66% and 4.2%, respectively. In addition, the pathway analysis to the second level shows that methylnaphthalene (C₁₀H₇CH₃) and methylnaphthalene radical (C₁₀H₇CH₂) are formed from the odd-carbon-atom pathways. For example, in the methylnaphthalene formation, phenyl plays an important role and mostly forms from propargyl, as discussed in Fig. 15. Another example as seen in the methylnaphthalene radical formation is that a major pathway is through the reaction of phenylacetylene radical

Reaction network for the formation of naphthalene:

- Phenyl radical + C_3H_3 → Naphthalene (1.31 %)
- Phenyl radical + C_3H_3 → Naphthalene (1.54 %)
- Phenyl radical + C_2H_2 → Naphthalene (0.61 %)
- Phenyl radical + H → Naphthalene (14.66 %)
- Naphthyl radical + CH_3 + C_2H_4 + H_2 + H_2O → Naphthalene (35.83 %)
- Naphthyl radical + C_2H_2 → Naphthalene (0.69 %)
- Naphthyl radical + H → Naphthalene (36.75 %)
- 1-Naphthyl radical + H → Naphthalene (0.51 %)
- 1-Naphthyl radical + CH_3 → Naphthalene (4.2 %)
- 2-Naphthyl radical + H + CH_3 + C_2H_4 + H_2 + H_2O → Naphthalene (62.83 %)
- 2-Naphthyl radical + H + CH_3 → Naphthalene (28.05 %)
- 2-Naphthyl radical + C_3H_3 → Naphthalene (5.88 %)
- 1-Naphthyl radical + CH_3 → Naphthalene (43.15 %)
- 2-Naphthyl radical + C_3H_3 → Naphthalene (34.29 %)
- 2-Naphthyl radical + H → Naphthalene (22.08 %)

Figure 17: Kinetic pathways of formation of (a) A₃ aromatics (anthracene, C₁₄H₁₀) and (b) A₃ aromatic radicals (anthracenyl, C₁₄H₉), showing percentage contributions through various reactions based on the POLIMI mechanism [68-71]. Conditions: *n*-butane, $X_F=0.29$, $X_{O_2}=0.90$, and $K=57\text{ s}^{-1}$. Solid arrows show the first level of path analysis and dashed arrows show the second level of path analysis.

Figure 18: Kinetic pathways of formation of (a) A₄ aromatics (pyrene, C₁₆H₁₀) and (b) A₄ aromatic radicals (pyrenyl, C₁₆H₉), showing percentage contributions through various reactions based on the POLIMI mechanism [68-71]. Conditions: *n*-butane, $X_F=0.29$, $X_{O_2}=0.90$, and $K=57\text{ s}^{-1}$. Solid arrows show the first level of path analysis and dashed arrows show the second level of path analysis.

For the naphthyl radical (C₁₀H₇) formation shown in Fig. 16(b), apart from the stabilizing inter-conversion reactions, the pathway originating from the phenyl contributes to 23%. Again, the phenyl mostly forms from the propargyl. The other important step of acetylene addition has

22.1% contribution through the reaction of $C_6H_4C_2H + C_2H_2 \rightarrow C_{10}H_7$. The phenylacetylene radical involved in this reaction is formed through the decomposition of methylnaphthalene radical, which is formed via a major propargyl pathway discussed earlier.

Figure 17(a) shows the results for the A_3 ring anthracene formation. It is seen that a minute 0.05% contribution is from the acetylene addition reaction of $C_{12}H_9 + C_2H_2 \rightarrow C_{14}H_{10} + H$. Further analysis to the second level shows that in this reaction, the biphenyl radical ($C_{12}H_9$) is formed through the reaction where the propargyl is added to the indenyl. The other pathway in the A_3 formation is from the A_4 aromatic pyrene ($C_{16}H_{10}$), which is shown in Fig. 18(a) to originate from the reactions involving propargyl. In addition, the pathway of acenaphthyleneradical ($C_{12}H_7$) reacting with the propargyl, $C_3H_3 + C_{12}H_7 \rightarrow 0.5C_{14}H_{10} + 0.5C_{16}H_{10}$, contributes to 0.63%. Hence, the dominance of the propargyl can be seen in the A_3 formation as well. Similarly, the anthracenyl ($C_{14}H_9$) formation, as shown in Fig. 17(b), involves the propargyl pathways. From Fig. 18(a), it can be observed that, apart from the stabilizing inter-conversion reactions, the A_4 ring pyrene formation is mainly through the reaction pathways that include propargyl, while the acetylene has 0.57% contribution from the acetylene addition reaction of $C_{14}H_9 + C_2H_2 \rightarrow C_{16}H_{10} + H$. It is also noted in the POLIMI mechanism that the pyrenyl ($C_{16}H_9$) formation is mostly governed by the inter-conversion stabilization pathways, as shown in Fig. 18(b).

For the binary fuel blends studied here, the above-mentioned important reactions are expected to show more contributions in the PAH formation, as the experimental results demonstrated the synergistic effects. Although at the inception stage the role of propargyl should be the dominant determinant of the PAH formation [90,82], other pathways from the acetylene cannot be entirely ruled out [10-15]. As previously shown in Figs. 11-14, the calculated peak

mole fractions of the propargyl, benzene, naphthalene, anthracene, and pyrene increase with increasing β , but that of the acetylene decreases as the amount of straight chain isomer decreases. From the path analyses, it is clear that the major PAH pathways in the POLIMI mechanism [68-71] basically involve the odd-carbon-atom pathways. However, the experimental results from Fig. 10 show the synergistic effects, which are not predicted by the simulations. This discrepancy could be explained by the possibility that the acetylene addition reactions, as well as those beyond the HACA mechanism, also have significant contributions in the PAH formation. Based on the current experimental findings, it is suggested that the increased contributions of the acetylene addition reactions in the PAH formation can improve the comprehensiveness of the underlying reaction mechanism. To further develop these PAH-related chemistries to predict the larger aromatic ring PAHs, beyond the current A₄-ring in the POLIMI mechanism [68-71], the inclusion of the acetylene addition reactions (and possibly other new pathways) for the larger PAHs should be considered important, at least for the straight chain fuels.

5. Conclusions

Atmospheric pressure, non-premixed, sooting flames of the butanes and the butanols in the counterflow configuration were investigated to study the PAH formation, by using an optical diagnostic technique of planar laser-induced fluorescence for qualitative measurements of the PAHs with different aromatic ring sizes. The fuel structure effects on the PAH formation were observed, as within the same isomeric class the PAH formation tendencies differ. At the inception stage, the dominance of the propargyl pathways in the PAH formation was discussed based on the present experimental data and the simulated results using the POLIMI mechanism [68-71]. At the growth stage, the PAH formation ranking for the large PAHs formed just before

the formation of soot particles was found to be consistent with the sooting tendency determined based on the peak soot volume fraction measured by the laser-induced incandescence (LII) technique. Additional experiments were conducted for the binary fuel blends by blending the branched chain isomer with the baseline straight chain isomer. Such experimental results revealed some synergistic effects and suggested the importance of the acetylene addition pathways to account for the synergy, which, however, were not shown in the simulations. It was further found through the path analyses that the contribution of the HACA mechanism in the PAH formation described in the POLIMI mechanism [68-71] plays a minimal role. Hence, in addition to the odd-carbon-atom pathways of PAH formation, the importance of the HACA routes, as well as other pathways beyond the HACA mechanism, for the large PAH formation should be considered in the chemical kinetic models, especially for the straight chain fuels.

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References

- [1] I. Glassman, Soot formation in combustion processes, Symp. (Int.) Combust. 22 (1989) 295–311.
- [2] R.L. Vander Wal, K.A. Jensen, M.Y. Choi, Simultaneous laser-induced emission of soot and polycyclic aromatic hydrocarbons within a gas-jet diffusion flame, Combust. Flame 109 (3) (1997) 399–414.
- [3] P.T. Reilly, R.A. Gieray, W.B. Whitten, J.M. Ramsey, Direct observation of the evolution of the soot carbonization process in an acetylene diffusion flame via real-time aerosol mass spectrometry, Combust. Flame 122 (1-2) (2000) 90–104.
- [4] H. Richter, J.B. Howard, Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways, Prog. Energ. Combust. Sci. 26 (4-6) (2000) 565–608.
- [5] S. Senkan, M. Castaldi, Formation of polycyclic aromatic hydrocarbons (PAH) in methane combustion: Comparative new results from premixed flames, Combust. Flame 107(1–2) (1996) 141–150.
- [6] H. Hepp, K. Siegmann, K. Sattler, New aspects of growth mechanisms for polycyclic aromatic hydrocarbons in diffusion flames, Chem. Phys. Lett. 233 (1995) 16–22.
- [7] H. Bohm, M. Braun-Unkhoff, P. Frank, Investigations on initial soot formation at high pressures, Prog. Comput. Fluid Dyn. 3 (2003) 145–150.
- [8] N.M. Marinov, W.J. Pitz, C.K. Westbrook, A.M. Vincitore, M.J. Castaldi, S.M. Senkan, C. F. Melius, Aromatic and polycyclic aromatic hydrocarbon formation in a laminar premixed *n*-butane flame, Combust. Flame 114 (1-2) (1998) 192–213.
- [9] M. Kamphus, M. Braun-Unkhoff, K. Kohse-Hoinghaus, Formation of small PAHs in laminar premixed low-pressure propene and cyclopentene flames: Experiment and modeling, Combust. Flame 152 (1-2) (2008) 28–59.
- [10] M. Frenklach, J. Warnatz, Detailed modeling of PAH profiles in a sooting low-pressure acetylene flame, Combust. Sci. Technol. 51 (1987) 265–283.
- [11] 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.
- [12] M. Frenklach, Reaction mechanism of soot formation in flames, Phys. Chem. Chem. Phys. 4 (2002) 2028–2037.
- [13] M. Frenklach, H. Wang, Detailed modeling of soot particle nucleation and growth, Symp. (Int.) Combust. 23 (1991) 1559–1566.

- [14] M. Frenklach, H. Wang, Detailed Mechanism and Modeling of Soot Particle Formation, Springer-Verlag, New York, NY, 1994.
- [15] J. Appel, H. Bockhorn, M. Frenklach, Kinetic modeling of soot formation with detailed chemistry and physics: laminar premixed flames of C₂hydrocarbons, Combust. Flame 121 (2000) 122–136.
- [16] M.B. Colket, D.J. Seery, Reaction mechanisms for toluene pyrolysis, Symp. (Int.) Combust. 25 (1994) 883–891.
- [17] A. D’Anna, A. Violi, A kinetic model for the formation of aromatic hydrocarbons in premixed laminar flames, Symp. (Int.) Combust. 27 (1) (1998) 425–433.
- [18] A. D’Anna, J.H. Kent, A model of particulate and species formation applied to laminar, nonpremixed flames for three aliphatic-hydrocarbon fuels, Combust. Flame 152 (2008) 573–587.
- [19] J.A. Miller, S.J. Klippenstein, Y. Georgievskii, L.B. Harding, W.D. Allen, A.C. Simmonett, Reactions between resonance-stabilized radicals: Propargyl + allyl, Phys. Chem. A. 114 (2010) 4881–4890.
- [20] N. Hansen, J.A. Miller, S.J. Klippenstein, P.R. Westmoreland, K. Kohse-Hoinghaus, Exploring formation pathways of aromatic compounds in laboratory-based model flames of aliphatic fuels, Combust. Explo. Shock 48 (2012) 508–515.
- [21] A.M. Dean, Detailed kinetic modeling of autocatalysis in methane pyrolysis, J. Phys. Chem. 94 (1990) 1432–1439.
- [22] N.M. Marinov, W.J. Pitz, C.K. Westbrook, M.J. Castaldi, S.M. Senkan, Modeling of aromatic and polycyclic aromatic hydrocarbon formation in premixed methane and ethane flames, Combust. Sci. Technol. 116 (1996) 211–287.
- [23] A. D’Anna, J.H. Kent, Aromatic formation pathways in non-premixed methane flames, Combust. Flame 132 (2003) 715–722.
- [24] H. Richter, W.J. Grieco, J.B. Howard, Formation mechanism of polycyclic aromatic hydrocarbons and fullerenes in premixed benzene flames, Combust. Flame 119 (1-2) (1999) 1–22.
- [25] M. Schenk, N. Hansen, H. Vieker, A. Beyer, A. Götzhäuser, K. Kohse-Höinghaus, PAH formation and soot morphology in flames of C₄ fuels, Proc. Combust. Inst. 35 (2) (2015) 1761–1769.
- [26] J.Y. Hwang, W. Lee, H.G. Kang, S.H. Chung, Synergistic effect of ethylene-propane mixture on soot formation in laminar diffusion flames, Combust. Flame 114 (1998) 370–380.

- [27] J.Y. Hwang, S.H. Chung, W. Lee, Effects of oxygen addition on soot formation in counter-flow ethylene flames and the role of C₃ chemistry, *Symp. (Int.) Combust.* 27 (1998) 1531–1538.
- [28] J.A. Cole, H.J. Ederer, U. Stabel, J.B. Howard, Formation mechanisms of aromatic compounds in aliphatic flames, *Combust. Flame* 56 (1) (1984) 51–70.
- [29] C.H. Wu, R.D. Kern, Shock-tube study of allene pyrolysis, *J. Phys. Chem.* 91 (24) (1987) 6291–6296.
- [30] C.S. McEnally, L.D. Pfefferle, Experimental assessment of naphthalene formation mechanisms in non-premixed flames, *Combust. Sci. Technol.* 128 (1997) 257–278.
- [31] M.J. Castaldi, N.M. Marinov, C.F. Melius, J. Huang, S.M. Senkan, W.J. Pitz, C.K. Westbrook, Experimental and modeling investigation of aromatic and polycyclic aromatic hydrocarbon formation in a premixed ethylene flame, *Symp. (Int.) Combust.* 26 (1) (1996) 693–702.
- [32] C.S. McEnally, L.D. Pfefferle, An experimental study in non-premixed flames of hydrocarbon growth processes that involve five-membered carbon rings, *Combust. Sci. Technol.* 131 (1998) 323–344.
- [33] K.C. Smyth, J.H. Miller, R.C. Dorfman, W.G. Mallard, R.J. Santoro, Soot inception in a methane/air diffusion flame as characterized by detailed species profiles, *Combust. Flame* 62 (1985) 157–181.
- [34] B.S. Haynes, H. Jander, H.G. Wagner, Optical studies of soot formation processes in premixed flames, *B. Bunsenges. Phys. Chem.* 84 (1980) 585–592.
- [35] G. Prado, A. Garo, A. Ko, A. Sarofim, Polycyclic aromatic hydrocarbon formation and destruction in a laminar diffusion flame, *Symp. (Int.) Combust.* 20 (1984) 989–996.
- [36] F. Beretta, A. D'Alessio, A. D'Orsi, P. Minutolo, UV and visible laser excited fluorescence from rich premixed and diffusion flames, *Combust. Sci. Technol.* 85 (1992) 455–470.
- [37] R.J. Santoro, H.G. Semerjian, R.A. Dobbins, Soot particle measurements in diffusion flames, *Combust. Flame* 51(1983) 203–218.
- [38] R.J. Santoro, H.G. Semerjian, Soot formation in diffusion flames: flow rate, fuel species, and temperature effects, *Symp. (Int.) Combust.* 20 (1984) 997–1006.
- [39] A. Gomez, M.G. Littman, I. Glassman, Comparative study of soot formation on the centerline of axisymmetric laminar diffusion flames: Fuel and temperature effects, *Combust. Flame* 70 (1987) 225–241.

- [40] M.G. Allen, K.R. McManus, D.M. Sonnenfroh, P.H. Paul, Planar laser-induced-fluorescence imaging measurements of OH and hydrocarbon fuel fragments in high-pressure spray-flame combustion, *Appl. Opt.* 34 (1995) 6287-6300.
- [41] R.L. Vander Wal, Onset of carbonization: Spatial location via simultaneous LIF-LII and characterization via TEM, *Combust. Sci. Technol.* 118 (3-4) (1996) 343-360.
- [42] B.D. Crittenden, R. Long, Formation of polycyclic aromatics in rich premixed acetylene and ethylene flames, *Combust. Flame* 20 (3) (1973) 359-368.
- [43] J.D. Bittner, J.B. Howard, Composition profiles and reaction mechanisms in a near-sooting premixed benzene/oxygen/argon flame, *Symp. (Int.) Combust.* 18 (1981) 1105-1116.
- [44] J.M. Smedley, A. Williams, K.D. Bartle, A mechanism for the formation of soot particles and soot deposits, *Combust. Flame* 91 (1) (1992) 71-82.
- [45] J.T. McKinnon, J.B. Howard, The roles of PAH and acetylene in soot nucleation and growth, *Symp. (Int.) Combust.* 24 (1992) 965-971.
- [46] J.T. McKinnon, E. Meyer, J.B. Howard, Infrared analysis of flame-generated PAH samples, *Combust. Flame* 105 (1996) 161-166.
- [47] X. Hui, A.K. Das, K. Kumar, C.J. Sung, S. Dooley, F.L. Dryer, Laminar flame speeds and extinction stretch rates of selected aromatic hydrocarbons, *Fuel* 97 (2012) 695-702.
- [48] X. Hui, C.J. Sung, Laminar flame speeds of transportation-relevant hydrocarbons and jet fuels at elevated temperatures and pressures, *Fuel* 109 (2013) 191-200.
- [49] P. Singh, X. Hui, C.J. Sung, Soot formation in non-premixed counterflow flames of butane and butanol isomers, *Combust. Flame* 164 (2016) 167-182.
- [50] L. Verstraete, A. Leger, The visible and ultraviolet absorption of large polycyclic aromatic hydrocarbons, *Astron. Astrophys.* 266 (1992) 513-519.
- [51] F. Beretta, V. Cincotti, A. D'Alessio, P. Menna, Ultraviolet and visible fluorescence in the fuel pyrolysis regions of gaseous diffusion flames, *Combust. Flame* 61 (3) (1985) 211-218.
- [52] I.R. Berman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, second ed., Academic Press, New York, 1971.
- [53] G. Zizak, F. Cignoli, G. Montas, S. Benecchi, R. Donde, Detection of aromatic hydrocarbons in the exhaust gases of a gasoline I.C. engine by laser-induced fluorescence technique, *Recent Res. Dev. Appl. Spectrosc.* 1 (1996) 17-24.
- [54] L. Petarca, F. Marconi, Fluorescence spectra and polycyclic aromatic species in a *n*-heptane diffusion flame, *Combust. Flame* 78 (3-4) (1989) 308-325.

- [55] S.M. Lee, S.S. Yoon, S.H. Chung, Synergistic effect on soot formation in counterflow diffusion flames of ethylene–propane mixtures with benzene addition, *Combust. Flame* 136 (4) (2004) 493–500.
- [56] K.C. Smyth, C.R. Shaddix, D.A. Everest, Aspects of Soot Dynamics as Revealed by Measurements of Broadband Fluorescence and Flame Luminosity in Flickering Diffusion Flames, *Combust. Flame* 111 (1997) 185–207.
- [57] A. Ciajolo, R. Ragucci, B. Apicella, R. Barbella, M. de Joannon, A. Tregosi, Fluorescence spectroscopy of aromatic species produced in rich premixed ethylene flames, *Chemosphere* 42 (5–7) (2001) 835–841.
- [58] L.A. Sgro, P. Minutolo, G. Basile, A. D'Alessio, UV-visible spectroscopy of organic carbon particulate sampled from ethylene/air flames, *Chemosphere* 42 (5–7) (2001) 671–680.
- [59] A. Ciajolo, R. Barbella, A. Tregossi, L. Bonfanti, Spectroscopic and compositional signatures of PAH-loaded mixture in soot inception region of a premixed ethylene flame, *Symp. (Int.) Combust.* 27 (1998) 1481–1487.
- [60] C.S. McEnally, L.D. Pfefferle, Experimental study of nonfuel hydrocarbons and soot in coflowing partially premixed ethylene/air flames, *Combust. Flame* 121 (4) (2000) 575–592.
- [61] F. Ossler, T. Metz, M. Aldén, Picosecond laser-induced fluorescence from gas-phase polycyclic aromatic hydrocarbons at elevated temperatures. I. Cell measurements, *Appl. Phys. B* 72 (2001) 465–478.
- [62] A. Ciajolo, A. Tregossi, R. Barbella, R. Ragucci, B. Apicella, M. de Joannon, The relation between ultraviolet-excited fluorescence spectroscopy and aromatic species formed in rich laminar ethylene flames, *Combust. Flame* 125 (4) (2001) 1225–1229.
- [63] B.C. Choi, S.K. Choi, S.H. Chung, Soot formation characteristics of gasoline surrogate fuels in counterflow diffusion flames, *Proc. Combust. Inst.* 33 (2011) 609–616.
- [64] Y. Wang, A. Raj, S.H. Chung, A PAH growth mechanism and synergistic effect on PAH formation in counterflow diffusion flames, *Combust. Flame* 160 (9) (2013) 1667–1676.
- [65] S.S. Yoon, S.M. Lee, S.H. Chung, Effect of mixing methane, ethane, propane, and propene on the synergistic effect of PAH and soot formation in ethylene-base counterflow diffusion flames, *Proc. Combust. Inst.* 30 (2005) 1417–1424.
- [66] in: *CHEMKIN-PRO, Reaction Design*: San Diego, 2011.
- [67] R.J. Kee, J.A. Miller, G.H. Evans, G.D. Lewis, A computational study of the structure and the extinction of strained, opposed flow, premixed methane-air flame, *Symp. (Int.) Combust.* 22 (1988) 1479–1494.

- [68] A. Frassoldati, A. Cuoci, T. Faravelli, E. Ranzi, Kinetic modeling of the oxidation of ethanol and gasoline surrogate mixtures, *Combust. Sci. Technol.* 182 (2010) 653-667.
- [69] A. Frassoldati, A. Cuoci, T. Faravelli, U. Niemann, E. Ranzi, R. Seiser, K. Seshadri, An experimental and kinetic modeling study of n-propanol and iso-propanol combustion, *Combust. Flame* 157 (1) (2010) 2-16.
- [70] A. Frassoldati, R. Grana, T. Faravelli, E. Ranzi, P. Obwald, K. Kohse-Hoinghaus, Detailed kinetic modeling of the combustion of the four butanol isomers in premixed low-pressure flames, *Combust. Flame* 159 (2012) 2295-2311.
- [71] A. Goldaniga, T. Faravelli, E. Ranzi, P. Dagaut, M. Cathonnet, Oxidation of oxygenated octane improvers: MTBE, ETBE, DIPE, and TAME, *Symp. (Int.) Combust.* 27 (1) (1998) 353-360.
- [72] F.A. Williams, *Combustion Theory*, Addison-Wesley, 1985.
- [73] K. Seshadri, F.A. Williams, Laminar flow between parallel plates with injection of a reactant at high reynolds number, *Int. J. Heat Mass Transf.* 21 (1978) 251-253.
- [74] T.S. Norton, F.L. Dryer, The flow reactor oxidation of C1–C4 alcohols and MTBE, *Symp. (Int.) Combust.* 23(1990) 179–185.
- [75] W. Tsang, Thermal stability of alcohols, *Int. J. Chem. Kinet.* 8 (1976) 173–192.
- [76] T.K. Choudhury, M.C. Lin, C.Y. Lin, W.A. Sanders, Thermal Decomposition t-Butyl Alcohol in Shock Waves, *Combust. Sci. Technol.* 71 (1990) 219–232.
- [77] N.M. Marinov, A detailed chemical kinetic model for high temperature ethanol oxidation, *Int. J. Chem. Kinet.* 31 (1999) 183–220.
- [78] J. Park, R.S. Zhu, M.C. Lin, Thermal decomposition of ethanol. I. Ab Initio molecular orbital/Rice–Ramsperger–Kassel–Marcus prediction of rate constant and product branching ratios, *J. Chem. Phys.* 117 (2002) 3224–3231.
- [79] B.H. Bui, R.S. Zhu, M.C. Lin, Thermal decomposition of iso-propanol: First-principles prediction of total and product-branching rate constants, *J. Chem. Phys.* 117 (2002) 11188–11195.
- [80] B. Yang, P. Obwald, Y. Li, J. Wang, L. Wei, Z. Tian, F. Qi, K. Kohse-Hoinghaus, *Combust. Flame* 148 (4) (2007) 198–209.
- [81] J.T. Moss, A.M. Berkowitz, M.A. Oehlschlaeger, J. Biet, V. Warth, P.-A. Glaude, F. Battin-Leclerc, An experimental and kinetic modeling study of the oxidation of the four isomers of butanol, *J. Phys. Chem. A* 112 (43) (2008) 10843–10855.

- [82] C.S. McEnally, L.D. Pfefferle, Fuel decomposition and hydrocarbon growth processes for oxygenated hydrocarbons: butyl alcohols, *Proc. Combust. Inst.* 30 (1) (2005) 1363–1370.
- [83] P. Dagaut, S.M. Sarathy, M.J. Thomson, A chemical kinetic study of n-butanol oxidation at elevated pressure in a jet stirred reactor, *Proc. Combust. Inst.* 32 (1) (2009) 229–237.
- [84] G. Black, H.J. Curran, S. Pichon, J.M. Simmie, V. Zhukov, Bio-butanol: Combustion properties and detailed chemical kinetic model, *Combust. Flame* 157 (2) (2010) 363–373.
- [85] P. Oßwald, H. Guldenberg, K. Kohse-Hoinghaus, B. Yang, T. Yuan, F. Qi, Combustion of butanol isomers – A detailed molecular beam mass spectrometry investigation of their flame chemistry, *Combustion and Flame* 158 (2011) 2–15
- [86] K. Brezinsky, F.L. Dryer, A Flow reactor study of the oxidation of iso-butylene and an iso-nutylene/n-octane mixture, *Combust. Sci. Technol.* 45 (5) (1986) 225–232.
- [87] W. Tsang, J.A. Walker, Mechanism and rate constants for the reactions of hydrogen atoms with iso-butene at high temperatures, *Proc. Combust. Inst.* 22 (1989) 1015–1022.
- [88] N. Hansen, T. Kasper, S.J. Klippenstein, P.R. Westmoreland, M.E. Law, C.A. Taatjes, K. Kohse-Hoinghaus, J. Wang, T.A. Cool, Initial steps of aromatic ring formation in a laminar premixed fuel-rich cyclopentene flame, *J. Phys. Chem. A* 111 (19) (2007) 4081–4092.
- [89] J.A. Miller, M.J. Pilling, J. Troe, “Unravelling combustion mechanisms through a quantitative understanding of elementary reactions, *Proc. Combust. Inst.* 30 (1) (2005) 43–88.
- [90] J. Camacho, S. Lieb, H. Wang, Evolution of size distribution of nascent soot in n-and i-butanol flames, *Proc. Combust. Inst.* 34 (1) (2013) 1853–1860.