

# Formation of Polycyclic Aromatic Hydrocarbons (PAH) in Methane Combustion: Comparative New Results from Premixed Flames

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Direct sampling and GC/MS analysis of fuel-rich, laminar, premixed flames of methane indicates the production of higher in-flame peak concentrations of benzene and polycyclic aromatic hydrocarbons (PAH) than in the flames of ethane under similar combustion conditions. These findings are surprising and significant because the methane flame not only had a higher H/C ratio and lower carbon density, but also produced less acetylene and soot than the ethane flame. These results suggest the significance of species containing an odd number of carbon atoms in PAH formation processes in the methane flame, as well as the importance of soot surface reactions. Although aromatic and polyaromatic intermediates constitute trace by-products of combustion, their formation is of practical concern due to their potential adverse health effects.

## INTRODUCTION

Methane, the major component in natural gas, is generally believed to be the cleanest burning hydrocarbon fuel as it produces less CO<sub>2</sub> and more H<sub>2</sub>O than other fossil fuels because of its high H/C ratio [1, 2]. Another important aspect of methane combustion that contributed to its pristine image is the fact that its premixed flames with air do not soot; instead, they are blown out first because of flammability limit considerations [3]. However, in many other applications, such as in industrial power generators, heaters, and boilers, hydrocarbons are burned in diffusion-type flames, where fuel concentrations span a wide range from fuel-rich to fuel-lean conditions. In fuel-rich regions, the production of undesirable by-products including aromatic and polycyclic aromatic hydrocarbons (PAH) can occur. These pollutants can then be transported out of the main combustion core and emitted to the atmosphere. Because many of the PAHs formed are potentially toxic, carcinogenic, or mutagenic [4] and are believed to be precursors to soot formation, it is of considerable practical interest to compare the nature and levels of these by-products in methane combustion in relation to

those observed in the burning of other fossil fuels. In addition, there is growing interest to use natural gas as a supplement or a replacement for other fuels to reduce the emission of toxic by-products.

PAH levels in flames are conventionally determined by preconcentrating them on adsorbates such as Tenax and XAD resins, followed by solvent extractions, reconcentration, and GC/MS or HPLC analysis, which collectively can take anywhere from 24 to 48 hours to complete [5, 6]. In addition, the numerous sample transfer steps involved can result in PAH loss, thereby decreasing the reliability of these measurements. Recognizing these limitations, we developed a new accurate method that avoids most of the sample transfer steps associated with conventional methods [7]. In this approach, hot gases bearing PAHs are withdrawn from within the flame using a heated probe and transported to and directly analyzed by GC/MS. This direct analysis approach permits the accurate determination of the identities and absolute concentrations of PAHs rapidly, in 30 minutes or less, and represents an improvement of productivity by nearly a factor 20. We subsequently used this method to determine the microstructures of methane [7], ethane [8], propane, and ethylene flames [9]. In each case over 40 major, minor, and trace species were quantified including a large number of aromatics and PAH.

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In this communication, we compare the levels of PAHs produced in the premixed flames of methane, ethane and propane. The major chemical features of methane combustion have been studied extensively in the past, both in premixed [10–13] and diffusion flames [14]. In a limited number of studies, the concentrations of some PAHs were also measured [11]. Similarly, the chemical structures of ethane flames [15–17] and propane flames [18–20] were also investigated, again with emphasis on major products formed. Surprisingly, however, PAH levels in methane flames have not been compared to other hydrocarbon fuels under similar combustion conditions to assess the relative production rates of PAH pollutants.

## EXPERIMENTAL

The sketch of the experimental system used is presented in Fig. 1. Briefly, atmospheric pressure, premixed laminar flat flames were stabilized over a 50-mm diameter porous bronze burner that was cooled with ethylene glycol to about 105°C. Flames were also protected from the ambient air by using a concentric shield gas of argon. All the flames were retained on

the burner surface by the use of ethylene-glycol-cooled quartz stabilizing coil that was positioned 40 mm from the burner surface. Sampling was accomplished by withdrawing gases from within the flame using a heated 6-mm OD quartz microprobe with an orifice diameter of about 0.150 mm at its tapered tip. The samples were transferred to a computer-controlled gas chromatograph/mass spectrometer (Hewlett-Packard 5890/5972A) for analysis through silica-lined steel tubing. Gases were immediately analyzed directly without preconcentration. The sampling system, which includes the probe, transfer lines, and GC valves, was maintained at 300°C and at subambient pressures to minimize the condensation and/or adsorption of PAHs on surfaces [21] and was also checked for possible catalytic activity by passing unburned gas mixture; none was detected. In addition, there were no deposits found in the probe after the experiments were completed.

Identification of species was accomplished by matching both the gas chromatographic retention times to pure components and mass spectral fragmentation patterns to standard MS libraries. Species concentrations were then de-

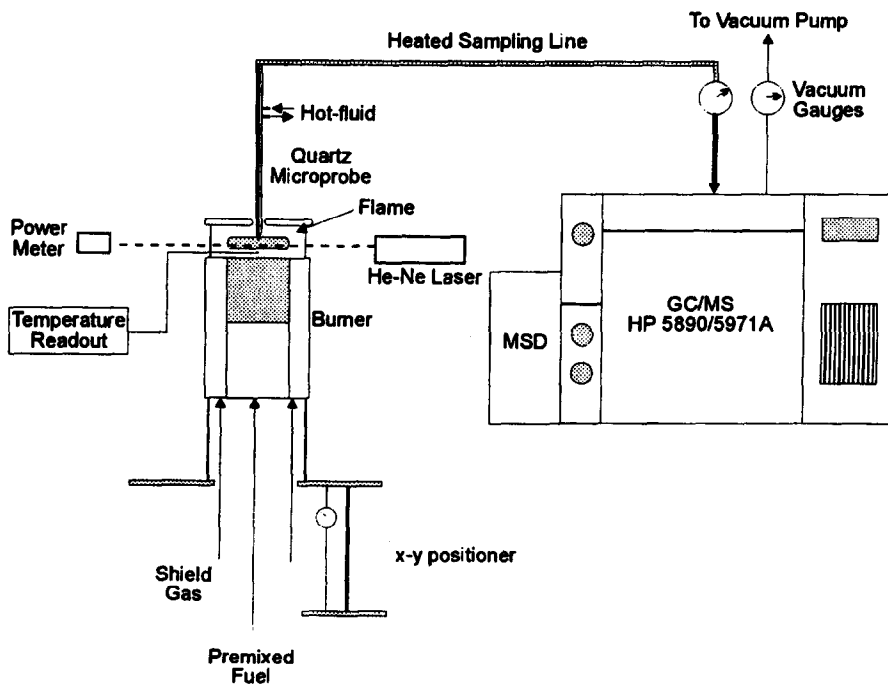


Fig. 1. Sketch of the experimental facility used.

terminated using calibration mixtures and by using argon as the internal standard. Species profiles were then generated by moving the burner relative to the stationary sampling probe with the aid of a vertical positioner having a precision of about 0.01 mm. Temperature profiles were measured using 0.075-mm Pt-Pt/13%Rh thermocouples coated with silica and vitrified after the completion of the composition measurements. The experiments were repeated several times to establish the reproducibility of our findings. Differences in measurements between different sets of experiments were about  $\pm 15\%$ .

Relative soot volume fractions were determined by passing a He-Ne laser beam (Uni-phase, 1508-0) through the center of the flame, and by recording the intensity of the transmitted light by a power meter. The burner was moved up and down to generate light transmission or extinction profiles, the latter being directly related to soot volume fraction [22].

For each flame, a total of nearly 45 distinct species were identified and concentration profiles for over 40 of them were determined. The species quantified include the usual light gases, Ar, H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, and C<sub>1</sub> through C<sub>18</sub> hydrocarbons. Since the presentation of all the results would be too lengthy, we shall concentrate on select PAH measurements in this report. The complete set of results for the methane and ethane flames are being published separately elsewhere [7, 8].

## RESULTS AND DISCUSSION

In Table I, the composition of the precombustion gas mixtures used and other features of the flames studied are summarized. As can be seen from this table, all the mixtures studied had the same equivalence ratio,  $\phi$ , of 2.50 [ $\phi = (\text{stoichiometric O}_2)/(\text{actual O}_2)$ ], and with the exception of ethane<sup>M</sup> flame, all had an argon dilution of about 45%. These fuel-rich flames were studied to enhance PAH formation such that they can be sampled and analyzed directly without preconcentration. The flames were positioned well above the burner surface under the conditions studied. As indicated in Table I, the flames possessed significantly different H/C, C/O ratios, and carbon densities. The methane flame had the highest H/C ratio of 4, compared to 3 for the ethane flame and 2.67 for the propane flame. The methane flame also had the lowest C/O ratio and carbon density of 0.62 and  $1.26 \times 10^{-5}$  mole/cc (1 atm and 298K), respectively. In comparison, the C/O ratios and carbon densities were 0.71 and  $1.86 \times 10^{-5}$  mole/cc for ethane, and 0.75 and  $2.25 \times 10^{-5}$  mole/cc for propane flames. Based on these parameters, one would expect that the methane flame should have the least propensity to form high molecular weight by-products. In addition to these studies, an experiment with another ethane flame that had the same carbon density as the methane flame was also conducted to

TABLE I  
Properties of the Flames Studied

Parameters	Methane Flame	Ethane Flame	Propane Flame	Ethane <sup>M</sup> Flame
Equivalence ratio, $\phi$	2.50	2.49	2.50	2.50
C/O ratio	0.62	0.71	0.75	0.71
Carbon density mole/cc at 298K	$1.24 \times 10^{-5}$	$1.86 \times 10^{-5}$	$2.25 \times 10^{-5}$	$1.25 \times 10^{-5}$
Cold gas velocity, cm/s	5.24	6.37	5.56	4.77
Feed composition (mole %)				
Ar	45.3	45.3	45.1	63.4
O <sub>2</sub>	24.3	32.0	36.6	21.3
CH <sub>4</sub>	30.4	—	—	—
C <sub>2</sub> H <sub>6</sub>	—	22.8	—	15.3
C <sub>3</sub> H <sub>8</sub>	—	—	18.3	—

better compare PAH levels produced in these systems. These experiments are designated as ethane<sup>M</sup>.

All the flames studied were sooting and exhibited a yellow-orange luminosity. Consequently, flame sampling had to be terminated when soot deposition plugged the probe orifice. This, however, occurred at a point farthest away from the burner surface, thus allowing the acquisition of flame structure information. Soot formation can complicate flame sampling because of possible retention of PAHs on probe and soot surfaces. However, at the sampling temperature of 300°C, all the PAHs reported here should remain in the gas phase based on vapor pressure considerations [21]. For example, for the case of pyrene, the largest PAH reported here, its vapor pressure would be about 190 torr at 300°C [21]. Since the highest partial pressure of pyrene observed in the experiments was of the order 0.006 torr, it would be safe to assume that this value represents

the bulk of the pyrene present in the system. Previous experimental investigations, where this issue was specifically addressed, support this point as well [23]. An examination of the probe interior as well as transfer lines after the experiments also indicates the absence of any tar-like deposits.

In Fig. 2, the temperature and laser light transmission profiles are presented as a function of distance along the reaction zone or above the burner. Lines were also drawn through the data points to illustrate trends. As evident from this figure, with the exception of the ethane<sup>M</sup> flame that only reached a peak temperature of about 1,100°C because of its high argon dilution, all the flames had similar maximum flame temperatures of about 1,200–1,250°C. The temperature rise in the methane flame was also slower. As also seen in Fig. 2, the amount of soot produced in the methane flame was lower than in the ethane flame, and that formed in the ethane flame was

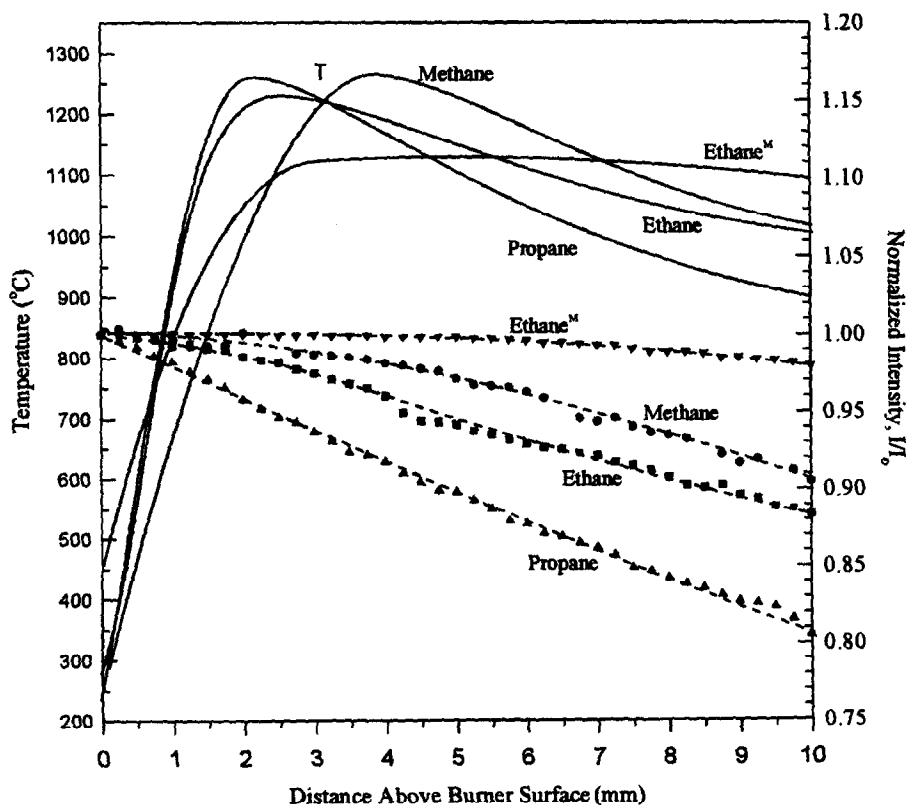


Fig. 2. The temperature and He-Ne laser light transmission intensity profiles along the methane, ethane, ethane<sup>M</sup>, and propane flames.

lower than in the propane flame. These results are not surprising and were expected based on our current understanding of hydrocarbon combustion. However, the amount of soot produced in the ethane<sup>M</sup> was lower than the methane flame.

In Fig. 3, mole fraction profiles of  $C_2H_2$  are compared to one another because of the generally believed association of acetylene with PAH and soot formation. As seen in Fig. 3, peak acetylene levels were about 4%, 3.5%, 2%, and 2% for propane, ethane, ethane<sup>M</sup>, and methane flames, respectively. This ranking is consistent with the soot levels presented in Fig. 2, and again supports the notion that methane combustion should produce the least amount of aromatic and polyaromatic hydrocarbon by-products. It is also interesting to note that acetylene levels in the ethane<sup>M</sup> flame were virtually identical to the methane flame.

In Fig. 4, the experimental mole fraction profiles for benzene ( $C_6H_6$ ) are presented. As evident from this figure, both ethane and propane flames produced benzene early on while its formation in the methane flame was delayed. This is consistent with the higher stand-off distance of the methane flame. However, benzene mole fractions in the methane flame subsequently increased rapidly along the reaction zone, and ultimately surpassed the levels observed in the ethane flame, and

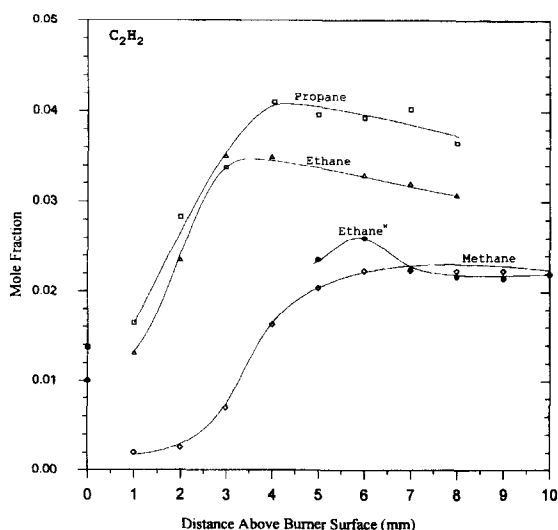


Fig. 3. Acetylene mole fraction profiles along the methane, ethane, ethane<sup>M</sup>, and propane flames.

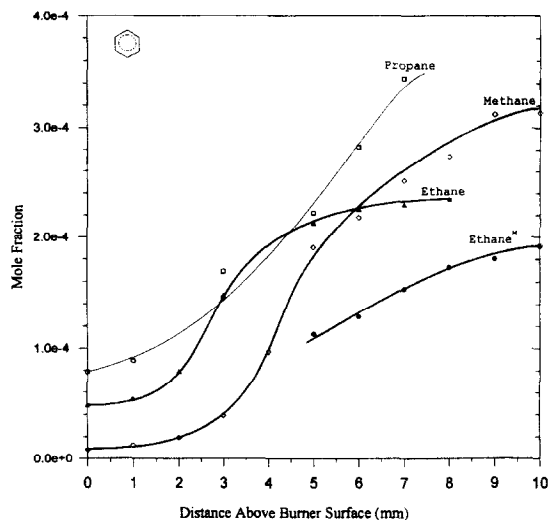


Fig. 4. Benzene mole fraction profiles along the methane, ethane, ethane<sup>M</sup>, and propane flames.

reached values as high as 325 ppm (parts per million by volume). In contrast, the peak benzene mole fraction was surprisingly lower at about 240 ppm in the ethane flame. It should be noted again that this occurs in spite of the lower acetylene and soot levels produced in the methane flame, as well as the lower carbon density and C/O ratio, and higher H/C ratio of the methane flame relative to the ethane flame. In the ethane<sup>M</sup> flame, which had the same carbon density as the methane flame, benzene mole fractions were lower over a longer flame distance with peak levels reaching about 200 ppm. Benzene levels in the propane flame were higher than the methane flame over the entire flame zone; this, however, was not a surprising result. A large number of substituted benzenes were also detected and quantified in these flames, and they exhibited trends similar to benzene [7].

In Fig. 5, the mole fraction profiles of naphthalene ( $C_{10}H_8$ ) are presented for each of the flames studied. Again, the levels of naphthalene produced in the methane flame exceeded the levels observed in the ethane flame, reaching values as high as 16 ppm. In contrast naphthalene levels peaked at 10 ppm in the ethane flame, and were lower in the ethane<sup>M</sup> flame over a longer flame distance. A variety of substituted naphthalenes were also generated in these flames, all behaving similar to

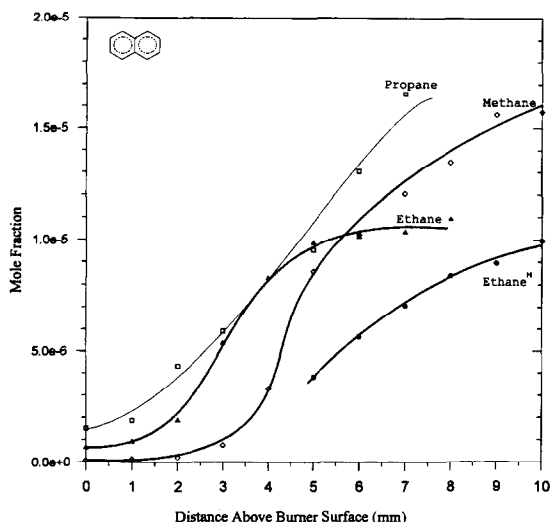


Fig. 5. Naphthalene mole fraction profiles along the methane, ethane, ethane<sup>M</sup>, and propane flames.

naphthalene [7]. As expected, naphthalene levels in the propane flame were higher than the methane flame.

In Fig. 6, the mole fraction profiles of phenanthrene ( $C_{14}H_{10}$ ) are compared. As evident from the figure, this 3-ring PAH reached levels as high as 4 ppm in both methane and propane flames, while peaking at lower levels of about 2.5 ppm in the ethane flame. The levels of phenanthrene in the ethane<sup>M</sup> flames

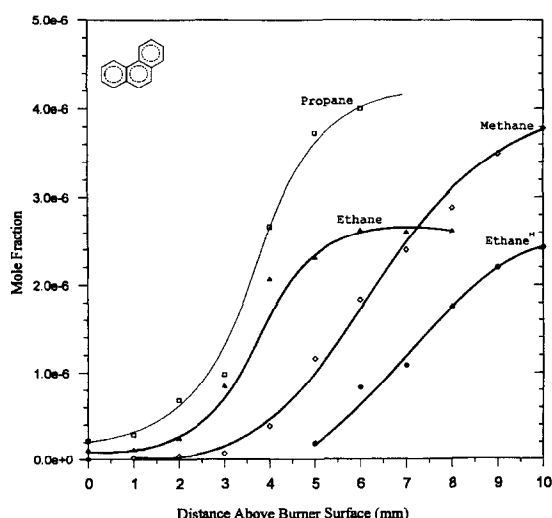


Fig. 6. Phenanthrene mole fraction profiles along the methane, ethane, ethane<sup>M</sup>, and propane flames.

were again lower than the methane flame over a longer flame distance. Anthracene, the isomer of phenanthrene, was also produced in all the flames studied, but at levels about a factor of 5 lower, and exhibited a similar trend.

Finally, the mole fraction profiles for pyrene ( $C_{16}H_{10}$ ), the largest PAH quantified in the present studies, are compared in Fig. 7. As can be seen from this figure, the behavior of the pyrene mole fraction profiles along the flames were similar to the other PAHs, with the methane flame producing significantly more of this intermediate than the ethane flame. Peak pyrene levels were about 7.5 and 4.8 ppm in the methane and ethane flames, respectively. As evident from Fig. 6, the levels of pyrene in ethane<sup>M</sup> flame were significantly lower than the methane flame. Fluoranthene, a  $C_{16}H_{10}$  isomer, was also produced in all the flames, at levels that were a factor of about 2 less than pyrene, and exhibited similar trends. From the comparison of the results presented in Figs. 5 and 6, it is interesting to note that the peak levels of 4-ring PAHs ( $C_{16}H_{10}$ ) formed in all the flames studied were significantly higher than the 3-ring PAHs ( $C_{14}H_{10}$ ).

The enhanced production of benzene and PAHs in the methane flame, relative to the ethane flame, is both surprising and significant for several reasons. First, the methane flame produced the least amount of soot and acety-

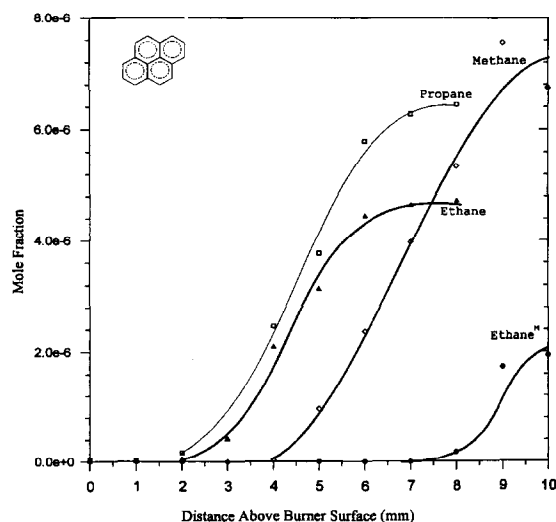


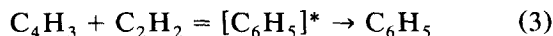
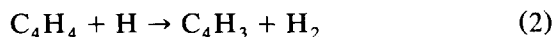
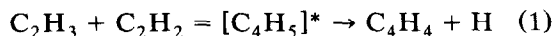
Fig. 7. Pyrene mole fraction profiles along the methane, ethane, ethane<sup>M</sup>, and propane flames.

lene, the latter being a species that is generally believed to be the key precursor to aromatics, PAH, and soot [22, 23]. Second, the methane flame not only possessed the highest H/C ratio of 4, but it also had the lowest carbon density of  $1.26 \times 10^{-5}$  mole/cc and the lowest C/O ratio of 0.62. In addition, because the rate of temperature rise in the methane flame was also slower than the ethane flame see Fig. 2), the production of aromatics at lower concentrations would have been expected based on recent numerical studies [24]. The increased production of benzene and 2-4 ring PAHs in the methane flame also suggest the increased production of even higher molecular weight PAHs; for example, the highly toxic benzo(a)pyrene [4, 25].

Since benzene and many PAHs are potentially toxic materials [4], our findings have an obvious significance for the assessment of the relative pollutant emissions from practical combustion systems burning methane (the major component of natural gas) and other hydrocarbon fuels, albeit at lower concentrations than those reported here. It should be noted again that the PAH levels determined in our fuel-rich premixed flames simulate the local PAH levels formed in turbulent diffusion flames that are commonly used practical combustion devices. In practical systems, eddies containing flamelets at different equivalence ratios (and therefore containing different levels of PAHs) can be transported away from the main combustion core, become quenched, and thus directly contribute to PAH emissions. These emissions, however, would be at much lower concentrations than the in-flame levels reported here because of dilution and other factors. Nevertheless, even these low levels of PAH emissions from combustion devices can dominate the risk factors induced by these devices [25, 26].

The increased production of benzene and PAHs in the methane flame compared to ethane can be explained by considering both the formation and removal reactions of these species. In some of the earlier mechanisms, aromatics have been suggested to form as a consequence of the reactions of species containing even number of carbon atoms, i.e.  $C_2H_x$  and  $C_4H_y$  [24, 27, 28]. In this case, benzene

and PAH have been proposed to form via sequences of hydrogen abstraction, acetylene addition reactions by Frenklach and coworkers [24, 27, 28]. This even number carbon route can be described, for example, by the following reaction sequence:



However, as indicated in Figure 3, acetylene concentrations in the methane flame were uniformly lower than the ethane flame, suggesting that reactions involving acetylene alone cannot account for the higher benzene and PAH levels formed in the methane flame relative to the ethane flame. Similarly, the levels of  $C_4H_2$  produced in flames, representing a dimerization product of  $C_2$  species, are shown in Fig. 8. Again the  $C_4H_2$  concentrations in the ethane flame were higher than the methane flame, indicating that the even number carbon route alone cannot account for the increased production of aromatics in the methane flame.

Our results suggest the importance of reactions that involve species having an odd number of carbon atoms such as  $CH_3$ [29] and  $C_3H_3$ [30] in the production of aromatics and

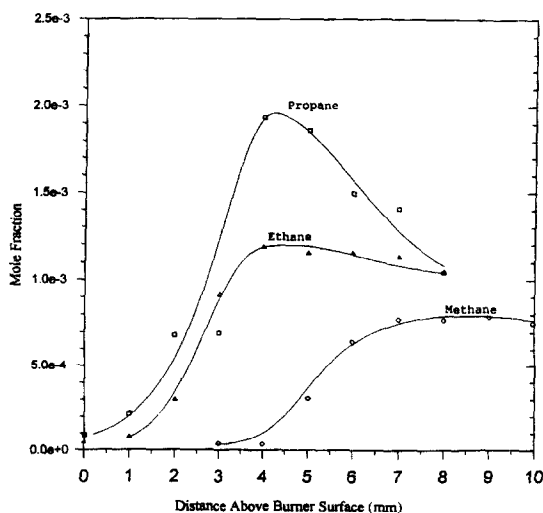
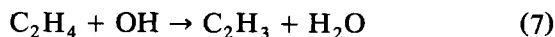
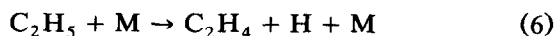
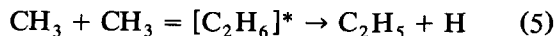
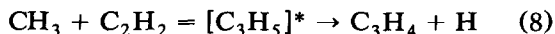


Fig. 8.  $C_4H_2$  mole fraction profiles along the methane, ethane, and propane flames.

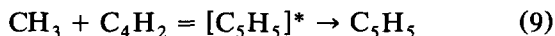
PAH. For example, methane flames naturally will have an abundance of  $\text{CH}_3$  radicals originating from the  $\text{CH}_4$  fuel, and these radicals are excellent building blocks for the synthesis of both even and odd carbon containing aromatic precursors. The recombination of  $\text{CH}_3$  radicals rapidly result in  $\text{C}_2\text{H}_6$  production, which, in turn, can lead to  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_3$  formation via reactions such as



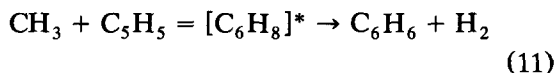
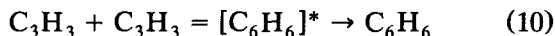
Alternately, the addition of abundant  $\text{CH}_3$  to  $\text{C}_2\text{H}_2$  can result in the production of  $\text{C}_3\text{H}_x$  as observed in the experiments:



$\text{C}_3\text{H}_3$  is then produced as result of further dehydrogenation of  $\text{C}_3\text{H}_4$ . Similarly,  $\text{CH}_3$  addition to  $\text{C}_4\text{H}_2$  would lead to  $\text{C}_5\text{H}_5$  formation, which upon hydrogenation produces  $\text{C}_5\text{H}_6$  that was also detected in the experiments:



Benzene formation can then occur by the recombination of  $\text{C}_3\text{H}_3$  radicals, as well as the recombination of  $\text{CH}_3$  and  $\text{C}_5\text{H}_5$ , i.e.,



In Fig. 9, the mole fraction profiles of  $\text{C}_3\text{H}_4$  are shown for the three flames investigated. As evident from these measurements,  $\text{C}_3\text{H}_4$  concentrations in the methane flame exceeded those observed in the ethane flame, thereby implicating its potential role in the molecular weight growth processes in the former flame. In fact, the  $\text{C}_3\text{H}_4$  levels followed a pattern similar to the benzene and PAH mole fraction profiles presented earlier in Figs. 4–7. In contrast, the aromatics would be expected to form primarily via the even carbon route in the ethane flame because  $\text{CH}_3$  radical concentrations are not expected to be as high as in the case of the methane flame. Similar (i.e., odd

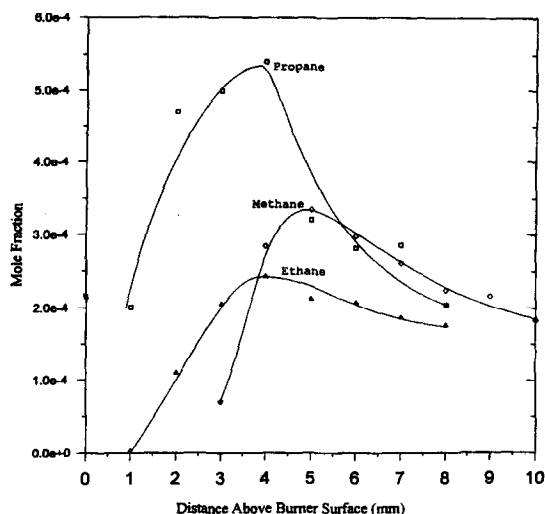
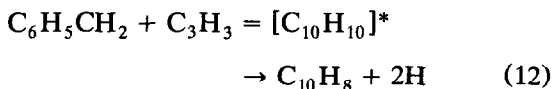
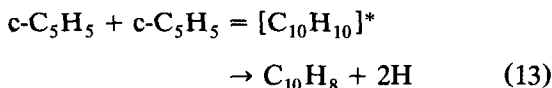


Fig. 9.  $\text{C}_3\text{H}_4$  mole fraction profiles along the methane, ethane, ethane<sup>M</sup>, and propane flames.

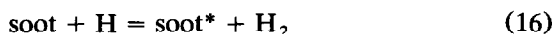
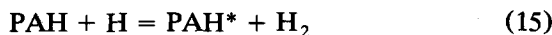
carbon) routes can also be devised to synthesize PAH as well. For example, naphthalene can be produced by [31]



as well as via the recombination of the cyclopentadienyl radicals (9):



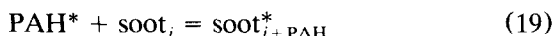
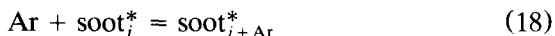
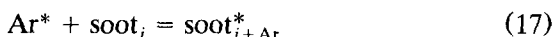
The higher levels of aromatics and PAH formed in the methane flame relative to the ethane flame can also be attributed to the reduced removal rates of these species from the gas phase by soot in the ethane flame. For example, it is well recognized that aromatics (Ar), PAH, and soot are activated via reactions such as [22, 23]



Once the activated  $\text{Ar}^*$ ,  $\text{PAH}^*$ , or  $\text{soot}^*$  are generated, aromatics and PAH can be removed from the gas phase through surface



reactions such as



In the methane flame, the rate of formation of activated species (i.e., reactions 14–16) would be expected to be slower than the ethane flame because of the presence of higher  $\text{H}_2$  partial pressures. This should also lead to reduced rate of soot formation, which, in return, would result in the maintenance of a greater fraction of the aromatics and PAH in the gas phase via reactions (17–20). In the case of the propane flame, the rates of production of aromatics and PAH evidently become so large that even higher soot levels could not remove them from the gas phase within the time scale of the experiments.

## CONCLUSION

The measurements of soot levels and PAH concentration profiles in the sooting premixed laminar flames of methane, ethane and propane have been accomplished by direct sampling and online GC/MS analysis. These measurements show a complex relationship between soot and PAH and that although the methane flame was the least sooting, the levels of aromatics and PAH produced were significantly higher than the ethane flame and were about the same as in the propane flame. Moreover, both the soot and PAH levels in the ethane flame that had the same carbon density as the methane flame were even lower.

These results are surprising as the methane flame not only possessed the highest H/C ratio, but also had the lowest C/O ratio and lowest carbon density among the flames studied, and produced the least amount of acetylene and soot. These findings provide significant new insights on the underlying chemical reaction pathways leading to the formation of PAH and soot in premixed laminar flames, and suggest the importance of species containing an odd number of carbon atoms in PAH formation processes in the methane flame, and the soot surface reactions.

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