**Study on sooting behavior of premixed C₁-C₄*n*-alkanes/air flames using
a micro flow reactor with a controlled temperature profile**

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Abstract

Sooting behavior of premixed C₁-C₄*n*-alkanes/air mixtures at maximum temperatures lower than 1400 K is studied experimentally using a micro flow reactor with a controlled temperature profile. Flame and soot responses to equivalence ratio (1.5 - 4.0) are observed for all mixtures. Critical sooting equivalence ratio observed for methane, propane and *n*-butane is 1.8, whereas, for ethane it is 1.9. Sooting behavior at similar critical equivalence is further interpreted qualitatively by observing relative axial locations of upstream edges of sooting region, where relative downstream location indicates delayed soot formation. The order of axial location of upstream edge of soot at equivalence ratio 1.8 is: propane < *n*-butane < methane; and, the order at equivalence ratio 1.9 is: propane ~ *n*-butane ~ ethane < methane. Sooting region shifts upstream for ethane, propane and *n*-butane with increasing equivalence ratio. However, it doesn't change for methane with increasing equivalence ratio above 2.0. One dimensional computations with detailed chemistry are performed to study observed flame and soot responses. Ethane is found to be most reactive fuel due to coupling of H abstraction from fuel and H production in the flame. Computed flame positions vary widely among mechanisms for methane. Most exothermic reaction at flame is $\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6$ for all mechanisms and for all the fuels. Computations using KAUST mechanism are performed for all the fuels at various equivalence ratios in the range 1.35 to 4.0 to discuss overall sooting behavior. Maximum computed pyrene mole fractions are used to study relative sooting behavior qualitatively as they correlate well with soot. The trends of maximum computed pyrene mole fractions qualitatively explain observed trends of critical sooting equivalence ratios and overall sooting behavior of fuels in the current experiments.

Keywords

Sooting behavior, Methane, Ethane, Propane, *n*-butane, Micro flow reactor

1. Introduction

Soot formation [1-3] has significant impact on air pollution. It also reduces the efficiency of combustion devices as it represents the un-oxidized carbon. Soot particles and PAHs (Polycyclic Aromatic Hydrocarbons) pose great health risks to us [4] which has led to stricter emission regulations on them. Thus, it becomes necessary to understand soot formation process in different operating conditions to develop technologies which aid clean and efficient utilization of hydrocarbon fuels.

Understanding soot formation in flames from first principles was realized due to pioneering works in the field [5-7] which led to need for developing reliable oxidation and PAH formation mechanisms to further the progress. Measurement of PAHs in flames [8–15] aided in understanding and development of chemical mechanism of PAH formation [15–24]. PAHs were theorized and now are widely accepted as precursors of soot. To compute soot, a HACA (hydrogen abstraction C_2H_2 addition) based mechanism for PAH and soot particle growth [18] was developed where soot was assumed to nucleate from pyrene and particle equations were solved using method of moments. Later, PAH species up to seven ring were modeled in gas phase and species heavier than pyrene were used to aid soot nucleation [25]. Effect of using heavier PAHs was shown to be important [26].

C_1 - C_4n -alkanes are major components of commercial gaseous fuels like CNG (Compressed Natural Gas) and LPG (Liquefied Petroleum Gas). Experiments with C_2 - C_4n -alkanes in premixed flames [3, 27-31] at maximum flame temperatures more than 1600 K concluded that sooting tendency increases with increasing fuel carbon number. Sooting tendency is usually characterized using critical sooting equivalence ratio or critical C/O ratio. Relative sooting tendency among fuels had been quantified using TSI (Threshold sooting Index) values. In premixed flames, TSI is defined as: $TSI = a - b * \varphi_c$, where φ_c is critical sooting equivalence ratio and a and b are device dependent constants. Lower TSI value (higher critical sooting equivalence ratio) means the fuel is less sooting. Lower TSI

value is assigned to methane compared to ethane [28-29], although critical sooting equivalence ratio for methane is reported to be lower for ethane [33]. Although, ethane produces more soot and less PAHs than methane at equivalence ratio of 2.5 in a premixed flame of maximum temperature around 1500 K [11]. The equivalence ratio dependence of relative sooting tendency between ethane and methane needs to be studied.

Studies on effect of temperature on sooting [32-34] conclude that sooting tendency increases with decreasing temperature below 1600 K. Experiments on sooting behavior of alkanes at lower temperatures, though, are rare [35–36] because sooting studies often utilize flames, whose maximum temperature is difficult to be dropped below 1500 K due to flammability issues in conventional premixed flame apparatus. Critical sooting equivalence ratios for ethane, ethylene and acetylene had also been successfully computed using detailed chemistry for PAH formation [37]. However, there is lack in information on both, experimental and computational relative sooting tendency among alkanes at temperatures below 1500 K. Effect of oxygen addition in counterflow and co-flow diffusion flames has been studied over range of effective equivalence ratios from 3 to infinity [38-39]. It is found that oxygen addition suppresses soot formation in methane but enhances soot formation in propane and *n*-butane [39]. In premixed flames, increasing equivalence ratios is supposed to increase sooting tendency. However, experimental investigations in premixed flames for wide range of equivalence ratios at temperatures below 1500 K ranges are not reported in literature. Practical range of temperature and equivalence ratio would vary widely depending on the combustor and its operating conditions. Experiments and computations in a micro flow reactor with a temperature gradient can provide crucial information regarding sooting tendency of fuels at lower temperatures and wide range of equivalence ratios.

A micro flow reactor with a controlled temperature profile [40-43] has been developed through research on micro-combustion. It has served as a simple and useful tool to study flame chemistry

[43-50]. It consists of a quartz reactor tube whose inner diameter is less than quenching diameter of the test mixture. The reactor is heated by an external heat source which creates a stationary temperature profile along the inner wall of reactor. Due to larger heat capacity of reactor and low gas flow rates inside the reactor which lead to small Peclet number, gas temperature depends strongly on wall temperature. Weak flames have been used to study ignition and oxidation characteristics of many fuels [43-50]. Radical quenching was found to have negligible effect on flame behavior under current conditions in a micro flow reactor [51] and a micro-channel [52]. The micro flow reactor has also been used to study sooting behavior and PAH formation in fuels [53-54].

It is recognized that temperature time history in the flames should be similar in the measurements for meaningful comparison of sooting tendency among fuels [30]. In earlier works on sooting tendency measurements adiabatic flame temperature of flame was controlled using nitrogen dilution [30, 33]. The micro flow reactor provides a new way to control temperature profile in premixed flame systems. Current experimental method excludes the need to account for dilution and could provide thermally similar conditions for sooting tendency comparison among fuels. The micro flow reactor also enables the experiments beyond usual lean and rich flammability limits.

Current work aims to study experimental sooting behavior of methane, ethane, propane and *n*-butane using a micro flow reactor with a controlled temperature profile of maximum temperatures lower than 1500 K and wider range of equivalence ratios. Computations are performed to understand correlation between PAHs and soot. Relative sooting behavior of fuels is discussed based on computed PAH mole fractions.

2. Experimental method

A schematic of micro flow reactor's experimental setup is presented in Fig. 1. The setup employed a quartz reactor tube with an inner diameter of 2 mm. The reactor tube was heated externally by a premixed hydrogen/air flat-flame burner. Hydrogen was used as fuel in external heater as it aids in better observation of chemiluminescence from flame and thermal radiation from soot in the reactor. External heating created a stationary temperature profile along the inner wall of reactor termed wall- temperature profile.

The wall-temperature profile along the inner surface of the reactor was measured by a K-type thermocouple inserted from the downstream end of reactor before experiments and is shown in fig. 2. Maximum temperature in the reactor was 1330 K. The effect of airflow on measured temperature profile was negligible for mean inlet velocity considered in current experiments.

The purity of each fuel used was more than 99.9 %. The equivalence ratio of the fuel air mixture was varied from 1.5 to 4.0. The fuel and air were supplied to the reactor at inlet velocity of 10 cm/s. Reynolds number in experiment is of the order of 10, so, the flow is laminar and turbulence is not expected to influence any observations. The flow rates of fuel and air were controlled using two different mass flow controllers and fuel and air were mixed before entering the reactor test section. Air was passed before each experiments to ensure the oxidation of residual soot from reactor wall from previous experiments. All experiments were conducted at atmospheric pressure. The chemiluminescence from flame and thermal radiation from soot were observed using a digital still camera, Nikon D-800. The flame position in experiments is defined as the position of maximum luminosity from the flame.

3. Computational method

The flow inside microflow reactor was modeled as one-dimensional, steady-state reactive flow. Computations were conducted using a modified PREMIX [55] based code from CHEMKIN-PRO software (Release 15131). The code was modified using a user defined function to account for convective heat transfer between inner gas and reactor wall which resulted in addition of a heat convection term to gas-phase energy equation [40].

$$\dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^K \rho Y_k V_k c_{pk} \frac{dT}{dx} + \frac{A}{c_p} \sum_{k=1}^K \omega_k h_k W_k - \frac{A}{c_p} \frac{4\lambda Nu}{d^2} (T_w - T) = 0$$

Wall-temperature profile used in computations is derived from experimental measurements as shown in fig.2. The computational domain was 10 cm long. Computations were performed at same pressure and mean inlet velocity as experiments for all fuels at various equivalence ratios. Flame positions in the micro flow reactor were computed using GRI mech 3.0 [56], USC 2.0 [57] San Diego (Version 20141004) [58], ARAMCO 1.3 [59] and KAUST mech [19]. Methane flames were also computed using a chemical mechanism which includes PAH formation, proposed by Jin et al (called Jin mech hereafter) [22]. The flame position in the computations was defined as the peak of the heat release rate profile. KAUST mech [19], a detailed kinetic mechanism for PAH formation for C₁-C₄ fuels was used to compute aromatics formation.

Computation including soot modeling was performed for methane using method of moments to solve particle equations [25] at equivalence ratio of 1.8. These computations were used only as a reference to examine correlation between computational PAHs concentration and computational soot formation. Particle formation and growth mechanism proposed by Wang et al. [25] is used which also includes HACA growth. Particle aggregation and radiation from the particles were not considered. The particle equations coupled with gas phase equations were solved using a segregated solver scheme in CHEMKIN-PRO.

4. Results and discussion

4.1 Experimental sooting characteristics

Some experimental observations are presented at first to show classifications of observed flame and soot responses. Figure 3 shows representative direct images of various flame and soot responses of fuel and air mixture for equivalence ratio in the range 1.5 - 4.0. Four different kinds of flame and soot responses, namely FREI (Flames with Repetitive Extinction and Ignition) [40], flame (stable propagating flame), flame + soot (sooting region downstream of the flame) and soot (sooting region without flame) were observed. Figure 3a shows FREI for propane at $\phi = 1.5$. Figure 3b shows a normally propagating flame for ethane at $\phi = 1.7$. The flame is shown in a dotted circle in all images. Figure 3c shows flame + soot for *n*-butane flame at $\phi = 1.9$. Figure 3d shows soot for methane at $\phi = 4.0$.

Figure 4 summarizes all the flame and soot responses observed for fuel/air mixtures in an equivalence ratio-fuel plane. FREI is observed at lower equivalence ratios. On increasing equivalence ratio, a stationary flame is observed. The equivalence ratio over which FREI is observed increases with increasing carbon number of fuel. On increasing equivalence ratio further, soot appears downstream of flame. For methane, flame disappears and only soot is observed at equivalence ratio 3.0 and higher. Flame would disappear eventually for all fuels as maximum heat release (and thus CH concentration) decreases with increasing equivalence ratio, but is not observed in current range of equivalence ratio. These regions are depicted in fig. 4.

In current work, the critical sooting equivalence ratio, which is defined as lower equivalence ratio limit of the flame+soot regime, is found to be 1.8 for methane, propane and *n*-butane, and, 1.9 for ethane. Based on critical sooting equivalence ratio considerations, ethane would be less sooting than methane, propane and *n*-butane. This is different than the generally observed results, which indicate

increase in sooting tendency of fuels with increasing carbon number. C/O ratio, defined as ratio of number of carbon atoms to number of oxygen atoms in fuel and air mixture is one of the important parameters to characterize sooting flames of fuels. Critical sooting C/O ratios for methane, ethane, propane and *n*-butane are 0.45, 0.54, 0.54 and 0.55 respectively. Based on critical C/O ratio ethane, propane and *n*-butane would be similarly sooting and methane would be less sooting. Sooting tendency based on critical equivalence ratio and critical C/O ratios are found to be inconsistent with each other.

Sooting tendency of fuels at maximum temperature lower than 1400 K, presented in current experiments depend not only on C/O ratio (or equivalence ratio) of flame but also on chemical reactivity of fuel/air mixture which depends on C-H bond energy of concerned fuel. The reactivity of fuel decides the flame position in micro flow reactor, with more reactive fuels have flame situated at lower wall temperatures. Thus micro flow reactor enables us to explicitly observe the effect of fuel reactivity on soot formation. The micro flow reactor with a controlled temperature profile spatially separates oxidation, small aromatics formation and soot formation. This separation is possible due to small temperature gradient compared to convention premixed flames. Different phases of soot formation in a micro flow reactor is depicted here by taking an example of ethane flame at equivalence ratio of 2.0. At the flame, fuel decomposition and oxidation begins and C₂-C₄ aromatic precursors are formed. Just downstream of flame, small aromatics begin to form and increase in concentration downstream, leading to formation of PAHs and soot. The structure of sooting flames for other fuels can be explained similarly.

The position of sooting region in micro flow reactor depends on combined effect of fuel reactivity and rate of aromatics formation in concerned flame. Relative downstream location of sooting region

could indicate delay in soot formation which can be due to lower reactivity of fuel, lower rate of aromatics formation or combination of both effects. The upstream edge of sooting region is reproducible within 1 mm or within 10 K in terms of wall temperature. So, the relative position of axial location of upstream edge of sooting region among flames can be compared as an indicator of “relative ease of soot formation”. Sooting tendency in micro flow reactor is correlated to axial location of upstream edge of sooting region. However, it should be noted that soot yield is not measured directly and thus, sooting tendency comparison may not be quantitatively indicative of relative soot yields.

Observing direct flame images at critical sooting equivalence ratios provide further information about difference in sooting tendency of fuels having similar critical sooting equivalence ratio. Figure 6 shows direct images for flame and soot formation at equivalence ratio of 1.8 for all the fuels. It can be seen that ethane does not show thermal radiation from soot. Also, the order of axial location of upstream edge of soot at steady state for the other fuels is: propane < *n*-butane < methane. Thus, the order of sooting tendency at equivalence ratio of 1.8 is: methane < *n*-butane < propane. The difference in sooting tendency between propane and *n*-butane is much smaller compared to that between propane (and *n*-butane) and methane. The micro flow reactor identifies the difference in sooting tendency of fuels having similar critical sooting equivalence ratio.

Figure 7 shows direct images for flame and soot formation for fuels at equivalence ratio 1.9 which is critical sooting equivalence for ethane. The axial locations of upstream edges of sooting region are similar for ethane, propane and *n*-butane and are located upstream compared to that of methane. The downstream location of sooting region in methane is due to its lower reactivity leading to slower oxidation at 1300 K. Although, methane starts sooting at lower equivalence ratio (also, lower C/O ratio) than ethane, its sooting tendency is lower than ethane at equivalence ratios 1.9 and higher. At equivalence ratios higher than 1.9, the relative position of upstream edge of sooting region does not

vary among fuels. Thus, ethane has greater overall sooting tendency than methane if dependence on equivalence ratio is taken into account. Comparative sooting tendency between methane and ethane cannot be decided only by critical sooting equivalence ratio.

Figure 8 shows direct images for methane and *n*-butane at equivalence ratio 2.0, 3.0 and 4.0. The trends of upstream edge of sooting region for ethane and propane are similar to that for *n*-butane, thus, only *n*-butane case is shown here. The presented discussion regarding *n*-butane also applies to ethane and propane. Figure 8 shows effect of equivalence ratio on sooting region. The upstream edge of sooting region for methane does not change much with increasing equivalence ratio from 2.0 to 4.0, although, slight downstream shift is observed on increasing equivalence ratio from 2.0 to 3.0. The upstream edge of sooting region could not shift upstream due to low reactivity of methane at 1300 K and, so, no fuel oxidation is possible in the upstream region. It should also be noted that upstream edge of sooting region shifts upstream on increasing equivalence ratio from 1.8 to 2.0. It would imply that sooting tendency of methane doesn't increase with increasing equivalence ratio beyond 2.0. Also, flame is not observed for equivalence ratios 3.0 and 4.0. In an earlier work [8], it has been shown that soot and its precursors increase in concentration with increasing equivalence ratio at maximum temperature around 1600 K. The behavior of methane flame with increasing equivalence ratio in current experiments is not similar to [8] because of lower reactivity of methane at current temperatures. At maximum temperature above 1500 K the behavior of upstream edge of sooting region in methane flame should be similar to other fuels presented here. The upstream edge of sooting region for *n*-butane shifts upstream with increasing equivalence ratio, whereas flame position shifts downstream, slightly. However, the shift becomes smaller at higher equivalence ratios. The limiting position of upstream edge of sooting region is the flame position, as soot cannot form at locations where there is no fuel oxidation or dissociation. The decreasing distance between flame position and upstream edge of soot is also indicative of increased rate of aromatics formation with

increasing equivalence ratio. It can be inferred that sooting tendency of *n*-butane increases with increasing equivalence ratio.

4.2 Flame positions: experiments and computations

In the sooting conditions thermal radiation from soot is observed downstream of the flame for all fuels. Thus it is important for a mechanism to accurately predict flame positions in fuel rich conditions. In this section computations for flame positions prior to soot formation are presented for all fuels employed. Capability of various mechanisms to predict flame positions for all fuels are tested. All fuels show single luminosity peaks at flame in experiments and correspondingly single heat release peaks in computations. Reactions which significantly affect heat release at flames and thus the flame positions are then discussed with regards to various mechanisms for all fuels.

4.2.1 Methane

Figure 9 shows experimental flame position along with computed heat release rate profiles for methane at equivalence ratio of 1.7 using various mechanisms. Please note that this image is taken using a CH filter. Experimental flame position is at axial location of 6.40 cm where wall temperature is 1280 K. The computations using GRI mech 3.0 and San Diego mechanisms show maximum heat release rate at 6.39 cm and 6.55 cm where wall temperatures are 1278 K and 1299 K respectively. The computations with KAUST and USC 2.0 mechanisms show maximum heat release at 6.68 cm where wall temperature is 1309 K. USC 2.0 and KAUST mechanisms predict same flame position because KAUST mechanism is based on USC 2.0 mechanism. So, for further discussion, computations with USC 2.0 mechanism are not presented. The wall temperature at flame position is predicted within 30 K by GRI mech 3.0, San Diego and KAUST mechanisms. ARAMCO Mech predicts maximum heat release rate at 7.32 cm where wall temperature is 1327 K. Jin mech computes maximum heat release rate at 7.83 cm where wall temperature is 1325 K, thus

underpredicting the reactivity of methane which would also lead to significant underestimation of PAH mole fractions. The flame position prediction among the used mechanisms vary widely which indicates that methane oxidation reactions and their rates are not well understood and are widely debated.

Heat release at flame occurs mostly through radical recombination reactions in rich flames. Most exothermic reaction (reaction with highest positive heat release rate) at flame is: $\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$, for all mechanisms used in this work. The rate parameters (Collision frequency, A ; temperature index, n and activation energy, E) for this reaction differ among some mechanisms used here. Jin mech [22] uses same rate parameters as GRI mech 3.0 [56] and KAUST mechanism [19] uses same rate parameters as USC 2.0 [57]. In San Diego mech [58] this reaction is modeled only with a collision frequency, $n = 0$ and $E = 0$. Second most exothermic reaction at flame is: $\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$ according to USC 2.0, KAUST and ARAMCO mechanisms. This reaction is also important in GRI mech 3.0, Jin mech and San Diego mech in immediate downstream of respective computed flame. In computations with GRI mech 3.0 and Jin mech, second most important exothermic reaction is: $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$. Whereas San Diego mech predicts $\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$ as second most exothermic reaction. Most endothermic reaction (reaction with highest negative heat release rate) at flame is: $\text{C}_2\text{H}_4 + \text{H} (+\text{M}) = \text{C}_2\text{H}_5 (+\text{M})$, for all mechanisms used here.

4.2.2 Ethane

Figure 10 shows experimental flame position and computed maximum heat release profiles using various mechanisms for ethane at equivalence ratio of 1.7 and mean inlet velocity of 10 cm/s. In experiments the flame is located at axial location of 6.08 cm, where wall temperature is 1196 K. The computations with GRI mech 3.0 and San Diego mech show maximum heat release at 5.88 cm and 5.92 cm where wall temperatures are 1106 K and 1128 K respectively. KAUST mechanism predicts maximum heat release at 5.91 cm where wall temperature is 1124 K. ARAMCO mech computes

flame position at 5.99 cm where wall temperature is 1161 K. The flame positions computed using all mechanisms agree with experiments within 90 K. Agreement among various mechanisms in ethane is better than that for methane.

Similar to methane flames, most exothermic reaction at respective flame positions, as predicted by KAUST, ARAMCO and San Diego mechanisms is: $\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$. GRI mech 3.0 predicts the reaction: $\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$ as most exothermic reaction. This reaction is second most exothermic reaction as predicted by KAUST and ARAMCO mechanisms. GRI mech 3.0 computations show the reaction: $\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$ as second most exothermic reaction. Whereas, San Diego mechanism predicts the reaction: $\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$ as second most exothermic reaction but this reaction is not an important exothermic reactions in all other mechanism predictions. Most endothermic reaction at flames, as computed by all used mechanisms is: $\text{C}_2\text{H}_4 + \text{H} (+\text{M}) = \text{C}_2\text{H}_5 (+\text{M})$.

4.2.3 Propane

Figure 11 shows experimental flame position and maximum heat release rate profiles computed by various mechanisms for propane flame at equivalence ratio of 1.7 and mean inlet velocity of 10 cm/s. In experiments the flame is located at 6.23 cm where wall temperature is 1245 K. GRI mech 3.0 and San Diego mech compute flame positions at 6.00 cm and 6.17 cm respectively where wall temperatures are 1163 K and 1226 K respectively. KAUST mechanism predicts maximum heat release rate at axial location of 6.22 cm where wall temperature is 1243 K. The computation with ARAMCO mech shows maximum heat release rate at 6.22 cm where wall temperature is 1242 K. The flame position is predicted within 20 K by all mechanisms except GRI mech 3.0.

$\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$ is predicted as most exothermic reaction in KAUST, ARAMCO and San Diego mechanisms. GRI mech 3.0 predicts the reaction: $\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$ as most exothermic reaction and the reaction: $\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$ as second most exothermic

reactions. Computations using KAUST and ARAMCO mechanisms show the reaction: $\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$ as second most exothermic reaction. And, San Diego mechanism results show the reaction: $\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$ as second most exothermic reaction. Another important reaction for propane heat release in all mechanisms (except GRI mech 3.0) is: $\text{A-C}_3\text{H}_5 + \text{H} + (\text{M}) = \text{C}_3\text{H}_6 + (\text{M})$. Computations with KAUST and ARAMCO mech show the reaction: $\text{H} + \text{O}_2 = \text{O} + \text{OH}$, as most endothermic reaction at flame. Whereas, GRI mech 3.0 and San Diego mechanism results show the reaction: $\text{CH}_2\text{CHO} = \text{CH}_2\text{CO} + \text{H}$; this reaction is modeled with a third body in GRI mech 3.0.

4.2.4 *n*-butane

Figure 12 shows experimental flame position and computational maximum heat release rate profiles calculated by KAUST and ARAMCO mechanisms at equivalence ratio 1.8 and inlet velocity of 10 cm/s. In experiments the flame is located at axial position of 6.21 cm where wall temperature is 1239 K. Whereas, in computations by KAUST mechanism maximum heat release rate occurs at 6.12 cm where wall temperature is 1210 K. ARAMCO mech computes flame position at 6.19 cm where wall temperature is 1231 K. Flame position is predicted within 30 K by both mechanisms. KAUST and ARAMCO mechanisms predict the reaction: $\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$, as most exothermic reaction. KAUST mech shows the reaction: $\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$ as second most exothermic reaction. ARAMCO mech shows the reaction: $\text{HCCO} + \text{O}_2 = \text{CO}_2 + \text{CO} + \text{H}$ as second most exothermic reaction. Both KAUST and ARAMCO mechanism results show the reaction: $\text{C}_2\text{H}_4 + \text{H} (+\text{M}) = \text{C}_2\text{H}_5 (+\text{M})$ as most endothermic reaction at respective flame positions.

From these results, it can be seen that KAUST mechanism predicts comparative flame positions for all C_1 - C_4 fuels. Since KAUST mechanism also includes PAH formation reactions, it is used to discuss reactivity and overall sooting behavior of fuels in the following sections.

4.2.5 Analysis of higher reactivity of ethane

Analysis of relative flame positions of fuels reveal that ethane flame is located at lowest temperature, which indicates that ethane is most reactive among considered fuels. Higher reactivity for ethane in stoichiometric flames is attributed to higher rate of OH production in ethane flames and had been reported in detail earlier [49]. Here, higher reactivity of rich flames of ethane is discussed at equivalence ratio of 1.8. In rich flames, the fuel is mainly consumed through H and OH reactions with fuel with H abstraction by H radical being the dominant route. One of the three major reactions for H radical production in all fuels is: R249. $C_2H_4 + H(+M) = C_2H_5(+M)$. The rate of this reaction is about five times higher for ethane compared to the other fuels because C_2H_5 is produced by H abstraction from the fuel, C_2H_6 . The rates of other two reactions for H production do not show such wide variation among fuels. H abstraction from fuel and H production are coupled through fuel radical in ethane which increases fuel consumption at flame and thus increases its reactivity.

4.3 Correlating soot and A4: computations

Computations with soot modeling are performed for one reference case of methane at equivalence ratio of 1.8 to explain the reasoning behind choosing A4 to explain qualitative sooting tendency among considered fuels in later sections. Figure 13 shows computations for methane at equivalence ratio of 1.8 with and without soot modeling by KAUST mechanism. The profile of particle number density in computations including soot modeling begin rising when A4 mole fractions (in computations with and without considering soot modeling) start rising. The difference between pyrene mole fractions, with and without considering soot modeling increases as more soot particles are formed, but is negligible in the region where soot particles begin to form. Overall, the profile of A4 mole fractions are similar and correlate well with soot particle number density profile.

Figure 14 shows comparison between mass growth rate of particles by nucleation reaction of A4 and mass growth rate of particles considering all other reactions in the considered mechanism [25], for methane at $\phi = 1.8$. A4 nucleation reaction is: $2A_4 \Rightarrow 32C(B) + 20 H(se)$, where C (B) is carbon

particle and H(Se) is hydrogen site. All other reactions include three classes of reactions. First class of reactions consists of nucleation reaction of seven other PAHs (benzo(ghi)perylene, benzo(a)pyrene, benzo(e)pyrene, 1-ethynyl pyrene, 2-ethynyl pyrene, 4-ethynyl pyrene and coronene) which are considered for soot nucleation. Seven homogeneous nucleation reactions (e.g. $2\text{CORONEN} \Rightarrow 48\text{C(B)} + 24 \text{H(se)}$) and twenty eight heterogeneous nucleation reactions (e.g. $\text{A4} + \text{CORONEN} \Rightarrow 40\text{C(B)} + 22 \text{H(se)}$) are considered. Second class of reactions include HACA growth of soot particles (e.g. $\text{open(se)} + \text{C}_2\text{H}_2 \Rightarrow \text{H(se)} + 2\text{C(B)} + \text{H}$, here open(Se) is open site). Third class of reactions include PAH condensation reactions ($\text{A4} + 20\text{H(se)} \Rightarrow 16\text{C(B)} + 20\text{H(se)} + 5\text{H}_2$). It is observed that A4 dimerization is the main contributor to mass growth of particles and its contribution increases more rapidly compared to other reactions as A4 mole fractions increase downstream. So, A4 dimerization accounts for a minimum of 50% of the mass growth rate of particles and its contribution increases downstream. A4 dimerization rates depend on square root of temperature and A4 mole fractions, as A4 nucleation reactions are modeled with zero activation energy and temperature index of 0.5. The temperature is similar for all employed fuels at different equivalence ratios. So, A4 dimerization rate would mainly depend on A4 mole fractions.

Figure 15 shows computed mole fractions of A4 and sum of mole fractions of all other PAHs heavier than A4 which can be used in soot nucleation reactions for methane at $\phi = 1.8$ and propane at $\phi = 4.0$, considering only gas phase reactions. (All other PAHs include fluoranthene, chrysene, benzo(ghi)perylene, benzo(a)pyrene, benzo(e)pyrene, acepyrene, 1-ethynyl pyrene, 2-ethynyl pyrene, 4-ethynyl pyrene, perylene, anthanthrene and coronene.) The two flames considered here include two extremes. Methane flame at equivalence ratio of 1.8 is at critical sooting equivalence ratio, whereas, propane flame at equivalence ratio of 4.0 is highly sooting. It is observed that A4 mole fractions in both the flames are at least three times and mostly an order of magnitude higher than sum of all other higher PAHs combined. Hence, A4 mole fractions are used to qualitatively explain

overall sooting tendency of fuels in the current conditions. A4 mole fractions are chosen instead of computed soot volume fractions because soot formation in micro flow reactor can have unquantifiable uncertainties due to wall effects. Moreover, gaseous species like A4 can be measured and computed with certainty in the micro flow reactor in future experiments.

4.4 Sooting tendency of fuels: computational viewpoint

C/O ratio is an important parameter to characterize sooting tendency in fuels. In current experiments the critical C/O ratios for methane, ethane, propane and *n*-butane are 0.45, 0.54, 0.54 and 0.55, respectively. To understand sooting behavior in computations, dependence of maximum computed A4 mole fractions on C/O ratio is examined for all fuels. Figure 16 shows the variation of maximum computed A4 mole fractions with C/O ratio for all employed fuels. The maximum computed A4 mole fractions are analyzed as a function of C/O ratio. Although it should be noted that the reaction paths for PAH production from fuels depend on factors like chemical structure of fuel, its reactivity and temperature. Maximum computed A4 mole fractions for methane show different variation with C/O ratio compared to other fuels. For C/O ratios less than 0.55 methane has highest maximum computed A4 mole fractions whereas for C/O ratios greater than 0.55, the maximum computed A4 mole fractions for methane are lowest among all concerned fuels. The difference in maximum computed A4 mole fractions between methane and the other fuels is significant at most C/O ratios. It is also observed that maximum computed A4 mole fractions at same C/O ratios are similar for ethane, propane and *n*-butane. Although, a closer look reveals that ethane has slightly smaller A4 mole fractions compared to propane and *n*-butane. Maximum computed A4 mole fractions increase with increasing equivalence ratio for ethane, propane and *n*-butane. It should be noted that fig. 16 is plotted in log scale, so the difference is under-magnified at higher C/O ratios. These results imply

that C/O ratio cannot be treated as a comprehensive controlling factor to explain A4 productions for the four fuels in the current conditions and does not offer any additional advantage in characterizing these fuels compared to equivalence ratio. So, next, we look at variation of maximum computed A4 mole fractions with equivalence ratio which is one of the usual parameters to characterize premixed flames.

In experiments, ethane is found to start sooting at equivalence ratio of 1.9 whereas methane, propane and *n*-butane start sooting at equivalence ratio of 1.8. To examine this numerically, computations were performed for equivalence ratio in the range 1.35 to 4.0 for all fuels. Figure 17 shows the variation of maximum computed A4 mole fraction with equivalence ratio for all considered fuels. Maximum computed A4 mole fractions can be qualitatively linked to sooting tendency of fuels. It is seen that maximum computed A4 mole fractions for ethane are about an order of magnitude lower than those of methane, propane and *n*-butane at equivalence ratio below 1.8. To achieve a maximum mole fraction of order of 10^{-10} (chosen arbitrarily, although this number by itself makes no difference in conclusion), equivalence ratio for ethane is 1.5, whereas, for methane, propane and *n*-butane it is between 1.35 and 1.4. This result would indicate that methane, propane and *n*-butane have lower critical sooting equivalence ratio compared to ethane. Thus, trends of maximum computed A4 mole fractions qualitatively support the trend of critical sooting equivalence ratios observed in experiments. Although, quantitative comparison between experiments and computations cannot be done at this stage because measurements of gaseous PAH species are in preparation.

At equivalence ratio below 1.8, ethane shows least values of maximum computed A4 mole fractions. At equivalence ratio of 1.9, maximum computed A4 mole fraction for ethane is equivalent to that for methane. At equivalence ratios 2.0 and higher, maximum computed A4 mole fractions are lower for methane compared to that for ethane, propane and *n*-butane. Also, at equivalence ratios greater than 2.0, maximum computed A4 mole fractions decrease with increasing equivalence ratio

for methane. Ethane, propane and *n*-butane have similar variations of maximum computed A4 mole fractions with equivalence ratio, but, the differences in values of maximum computed A4 mole fractions among them increase with increasing equivalence ratio. These results qualitatively describe the trends of sooting tendency observed in experiments, as shown in Figs 4, 5 and 6.

To get further insights into lower production of A4 in ethane compared to other fuels, profiles of rate of A4 production are analyzed for all the fuels. Equivalence ratio of 1.7 is chosen for this analysis, because there is clear difference in maximum computed A4 mole fractions for ethane compared to other fuels, and it is lower than experimental critical sooting equivalence ratio for fuels, so, there will only be gas phase reactions. Figure 18 shows total rate of production of A4 for all concerned fuels at equivalence ratio 1.7. It is observed that ethane has lowest rate of production of A4. The integral value of total rate of production of A4 which is related to the overall production of A4 at the exit of reactor is lowest for ethane. The rate of production of A4 can also be viewed separately in flame region and post flame region for better comparison among fuels. The rates of production of A4 of propane and *n*-butane show significant peaks close to their flame positions, while, methane and ethane do not show distinctive peaks close to the respective flame positions. Rates of production of A4 in methane and ethane grow primarily in the post flame region, where methane grows at higher rate than other fuels. In the post flame region, too, ethane has lowest rate of production of A4. Thus, ethane has lowest mole fractions of A4 at the end of reactor in computations, as described earlier. A more detailed analysis to understand comparative reaction paths of C_1 - C_4n -alkanes will be subject of our future study which will include experimental mole fractions of PAHs.

4.4.1 Methane: Effect of equivalence ratio

Figure 19 shows experimental images for methane at equivalence ratios of 1.8 and 4.0 along with corresponding computations for heat release and A4 mole fraction profiles. Experiments show flame for equivalence ratio 1.8 but not for 4.0 whereas in computations it is seen as decrease in maximum heat release rate. At equivalence ratio of 4.0 the heat release rate profile is broader and indicates slow oxidation of methane.

In experiments, the sooting edge shifts upstream at equivalence ratio of 4.0 compared to 1.8. While in computations maximum A4 mole fractions decrease by three orders of magnitude. Weak oxidation and lower rates of thermal dissociation of methane creates lower concentration of radicals, thus, delays and reduces formation of PAHs significantly. This is in contrast to the experimental observations. The reason behind this can be due to two reasons. First, underestimation of reactivity and dissociation of methane in computation. Second, underestimation of PAH formation in computation. This signifies the need to model methane dissociation and PAH formation more accurately than we know at present.

4.4.2 Propane: Effect of equivalence ratio

Figure 20 shows experimental direct images for propane at equivalence ratio 1.8 and 4.0 along with corresponding computational profiles of heat release rate and A4 mole fractions. Ethane and *n*-butane have similar experimental images and computational profiles as this figure. So, here only propane is discussed. In computations, A4 mole fractions begin rising at flame. It is observed that with increasing equivalence ratio upstream edge of sooting region shifts upstream in experiments. In computations, A4 mole fractions increase with increasing equivalence ratio. Also, at upstream edge of soot the computed A4 mole fractions are higher at higher equivalence ratio.

This would be due to higher soot volume fractions at higher equivalence ratio. Soot nucleation reaction is usually modeled as a zero activation energy reaction with a collision efficiency. As soot formation increases, the number of unsuccessful collisions between nucleating species also increase.

Thus, there would be higher mole fractions of nucleating species (here A4) just upstream of sooting region at more sooting conditions. Alternatively, this problem can be seen as propagation of soot formation in a monotonic distribution of nucleating species concentration in a fixed one dimensional domain with varying rate of increase of nucleating species. In this case, steady state soot propagation limit is not decided by actual concentration of nucleating species. At higher rate of increase of nucleating species, soot propagation stops at higher concentration of nucleating species.

5. Conclusions

Sooting behavior of methane, ethane, propane and *n*-butane were studied using a micro flow reactor with a controlled temperature profile where maximum temperature is 1330 K. Four kinds of flame and soot responses are observed for fuels at mean inlet velocity of 10 cm/s and equivalence ratio ranging from 1.5 to 4.0 namely FREI, flame, flame + soot and soot. Critical sooting equivalence ratio observed for methane, propane and *n*-butane is 1.8, whereas that for ethane is 1.9. Axial locations of upstream edge of sooting region are observed at critical equivalence ratios to determine relative sooting tendency among fuels with similar critical equivalence ratio. The order of locations of upstream edge of sooting region, which can be viewed as an indicator of delay in soot formation, at equivalence ratio 1.8, is: methane < *n*-butane < propane; at equivalence ratio 1.9 the order is: methane < ethane ~ *n*-butane ~ propane. Upstream edge of sooting region doesn't shift with increasing equivalence ratio beyond 2.0 for methane, whereas, it shifts upstream for the other fuels. One dimensional computations are performed with detailed mechanisms for all fuels to compare computed flame positions with experiments. Ethane is found to be most reactive fuel due to coupling of H abstraction from fuel and H production. Most important exothermic and endothermic reactions at flame are $\text{CH}_3 + \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$ and $\text{C}_2\text{H}_4 + \text{H} (+\text{M}) = \text{C}_2\text{H}_5 (+\text{M})$ respectively. Computation using KAUST mech for equivalence ratio in range of 1.35-4.0 is performed to discuss qualitative sooting tendency of the fuels. Maximum computed A4 mole

fractions are lower for ethane compared to the other fuels at equivalence ratio below 1.8 which explains higher experimental critical sooting equivalence ratio for ethane. Also, maximum computed A4 mole fractions for methane show maximum at equivalence ratio of 2.0, whereas, those for ethane, propane and *n*-butane increase monotonically with increasing equivalence ratio. In experiments, upstream edges of sooting region do not change for methane with increasing equivalence ratio above 2.0 but those for ethane, propane and *n*-butane shift upstream with increasing equivalence ratio. KAUST mechanism qualitatively explains overall sooting behavior of the fuels in current conditions.

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Figure 1

Figure 1. A schematic of experimental setup.

Figure 2

Figure 2. Temperature profile measured in experiments and used in computations.

Figure 3

Figure 3. Representative direct images for flame and soot response of fuels at inlet velocity of 10 cm/s (a) FREI: propane, $\phi = 1.5$ (b) Flame: ethane, $\phi = 1.7$ (c) Flame + Soot: *n*-butane, $\phi = 1.9$ (d) Soot: methane, $\phi = 4.0$.

Figure 4

Figure 4. Overall flame and soot response for methane, ethane, propane and *n*-butane at $U_0 = 10\text{ cm/s}$ and $1.5 \leq \phi \leq 4.0$.

Figure 5

Figure 5. Phases of soot formation in a micro flow reactor demonstrated for ethane at $\phi = 2.0$ and $U_0 = 10$ cm/s.

Figure 6

Figure 6. Experimental direct images at equivalence ratio of 1.8 at mean inlet velocity of 10 cm/s for (a) methane (b) ethane (c) propane and (d) *n*-butane.

Figure 7

Figure 7. Experimental direct images at equivalence ratio of 1.9 at mean inlet velocity of 10 cm/s for (a) methane (b) ethane (c) propane and (d) *n*-butane.

Figure 8

Figure 8. Experimental direct images at mean inlet velocity of 10 cm/s for (a) methane and (b) *n*-butane for equivalence ratio of 2.0, 3.0 and 4.0.

Figure 9

Figure 9. Experimental flame position and computational heat release rate profile using different mechanisms for methane at $\phi = 1.7$ and $U_0 = 10$ cm/s.

Figure 10

Figure 10. Experimental flame position and computational heat release rate profile using different mechanisms for ethane at $\phi = 1.7$ and $U_0 = 10 \text{ cm/s}$.

Figure 11

Figure 11. Experimental flame position and computational heat release rate profile using different mechanisms for propane at $\phi = 1.7$ and $U_0 = 10$ cm/s.

Figure 12

Figure 12. Experimental flame position and computational heat release rate profile using different mechanisms for *n*-butane at $\phi = 1.8$ and $U_0 = 10$ cm/s.

Figure 13

Figure 13. Experimental direct image with computational particle number density and A4 mole fraction profiles for methane at $\phi = 1.8$.

Figure 14

Figure 14. Comparison between computational mass growth rate of particles by A4 dimerization and by other growth reactions for methane at $\phi = 1.8$.

Figure 15

Figure 15. Comparison between mole fraction profiles of A4 and other higher PAHs for methane at $\phi = 1.8$ and propane at $\phi = 4.0$.

Figure 16

Figure 16. Variation of maximum computed A4 mole fractions with C/O ratio for all fuels.

Figure 17

Figure 17. Variation of maximum computed A4 mole fractions with equivalence ratio for all fuels.

Figure 18

Figure 18. Total rate of production of A4 at $\phi = 1.7$ for methane, ethane propane and *n*-butane.

Figure 19

Figure 19. Direct images and computational profiles of heat release rate and A4 mole fraction for methane at $\phi = 1.8$ and $\phi = 4.0$.

Figure 20

Figure 20. Direct images and computational profiles of heat release rate and A4 mole fraction for propane at $\phi = 1.8$ and $\phi = 4.0$.