

Sooting Behavior of Ethane in a Micro Flow Reactor with a Controlled Temperature Profile

Ajit Kumar Dubey¹, Takuya Tezuka¹, Susumu Hasegawa¹, Hisashi Nakamura¹,
Kaoru Maruta^{1,2}

1: Institute of Fluid Science, Tohoku University, Sendai, Miyagi, Japan

2: ICE Lab., Far Eastern Federal University, Vladivostok, Russia

1 Introduction

Soot formation in combustion systems is more than often considered a nuisance as it decreases their efficiency and has negative effects on environment which also affects human health. Considering this, it is very important to understand the mechanisms, both physical and chemical, involved in soot formation. Soot, which is mostly carbon is formed during combustion of fuels at equivalence ratio sufficiently higher than unity. Soot formation is known to be dependent on fuel structure and operating conditions of the combustion device. C₂ hydrocarbons are most widely studied fuels for soot formation and a lot of studies have been done on modeling [1] for these fuels. Melton et al. [2] performed detailed PAH measurements for premixed flames of ethane and found that PAH species are very sensitive to mixture equivalence ratio. The concerned temperature for soot experiments were greater than 1600 K.

A micro flow reactor with a controlled temperature profile [3] is a simple device useful for studying reactive flow. In micro flow reactor, gas temperature depends strongly on the wall temperature profile due to small Peclet number, higher heat capacity of reactor tube and low amount of gas flowing in the reactor tube. The gas-phase temperature profile can be controlled externally which enables to capture flame physics and chemistry at desired temperatures. Nakamura et al. [4] used the micro flow reactor to study soot formation in methane and PAH formation process in acetylene, thus successfully demonstrating the usefulness of the micro flow reactor to study soot formation process. They also successfully showed the dependence of sooting limits on equivalence ratio and flow velocity (residence time and mass flow rate). The micro flow reactor was also employed to study soot formation in higher hydrocarbons, n-hexadecane and iso-cetane [5] and effect of fuel structure on sooting limits and PAH formation was studied. Difference in sooting behavior for straight and branch chain hexadecane was explicitly observed. Difference in reaction paths for formation of PAHs were also identified by measuring intermediate PAH species.

In the current work, soot formation in ethane (C₂H₆) is studied using the micro flow reactor to understand its sooting limits. The maximum temperature in current experiment is 1300 K which is lower than temperatures typically used in soot studies. Thus the setup provides for understanding sooting mechanism at lower and intermediate temperatures. Soot and flame response of ethane is studied for various equivalence ratio ($1.5 \leq \phi \leq 4.5$) and mean inlet velocity ($10 \text{ cm/s} \leq U_0 \leq 80 \text{ cm/s}$) conditions. These experiments clearly identify sooting limits of ethane and its dependence on

equivalence ratio and mean inlet velocity. Computations are also performed using a chemical mechanism recently proposed by Wang et al. [6] to understand the chemistry involved.

2 Experimental Setup

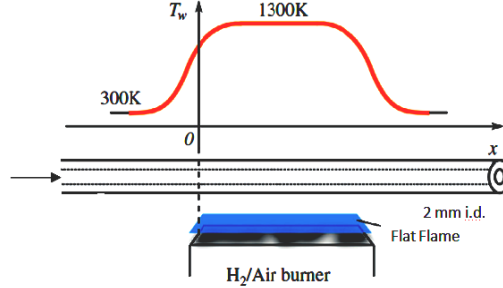


Figure 1. Experimental setup.

A micro flow reactor with a controlled temperature profile as shown in Fig. 1, employed a quartz tube whose inner diameter was 2 mm which is less than ordinary quenching diameter of given mixture. The reactor tube was heated externally by a premixed hydrogen-air flat flame burner to establish a stationary temperature profile along inner wall of tube. The temperature profile was measured along the inner surface of micro flow reactor using a thermocouple inserted from the exit before the experiments. In the current experiment maximum temperature was 1300 K. The maximum temperature difference between top and bottom portion of inner wall of reactor is around 30 K. The temperature profile measured along the bottom part of inner surface of micro flow reactor is called experimental wall temperature profile and is used in further discussions and computations. Air and fuel flows are metered by separate mass flow controllers. Air and fuel were mixed before entering the reactor. The flame images were taken using a digital still camera (Nikon D-300).

3 Computational method

The flow in micro flow reactor was modeled as one dimensional steady and reactive plug flow with convective heat transfer between inner gas to reactor wall included in energy equation [3][4][5].

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

Computations were performed using premixed flame model in CHEMKIN-PRO software with modification in energy equation by user defined function. Experimental wall temperature profile was used as T_w with a constant Nusselt number, Nu of 4 in the equation. The chemical mechanism proposed by Wang et al [6] for C_1 - C_4 hydrocarbons was used. It has 202 species and 1351 reactions and includes reactions for PAHs up to coronene ($C_{24}H_{12}$).

4 Results and discussion

Three different “flame and soot” responses are observed for ethane for various equivalence ratios ($1.5 \leq \phi \leq 4.5$) and mean inlet velocity ($10 \text{ cm/s} \leq U_0 \leq 80 \text{ cm/s}$) conditions, namely, flame (only a flame is observed), flame + soot (a flame is observed upstream of soot) and soot (only thermal radiation from soot is observed). With increasing equivalence ratios, the luminosity of flame decreases. Representative images are shown in Fig. 2 (left). The overall response is shown in fig. 2 (right). Below $\phi = 1.9$ soot is not observed for any flow velocity concerned here. For $1.9 \leq \phi \leq 2.2$ soot is observed at U_0 higher than a particular value which decreases as equivalence ratio increases. The equivalence ratio at which soot is first seen is called critical sooting equivalence ratio. Thus critical sooting equivalence

ratio decreases with increasing velocity. At higher equivalence ratio soot is observed for all U_0 concerned here. Only soot is seen at higher equivalence ratio and low mean inlet velocity.

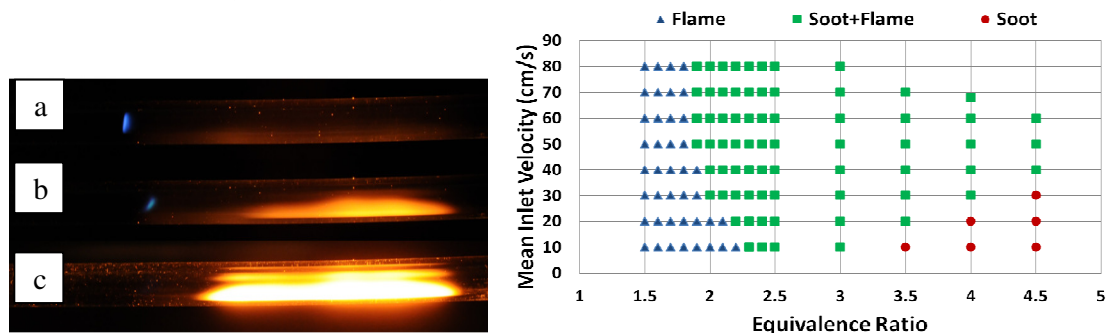


Figure 2. Left: Representative direct images for soot and flame response of ethane (a) Flame ($\phi = 1.5$, $U_0 = 40$ cm/s) (b) Flame + Soot ($\phi = 2.3$, $U_0 = 30$ cm/s) (c) Flame ($\phi = 4$, $U_0 = 10$ cm/s). Right: Overall soot and flame response of ethane on $\phi - U_0$ plane.

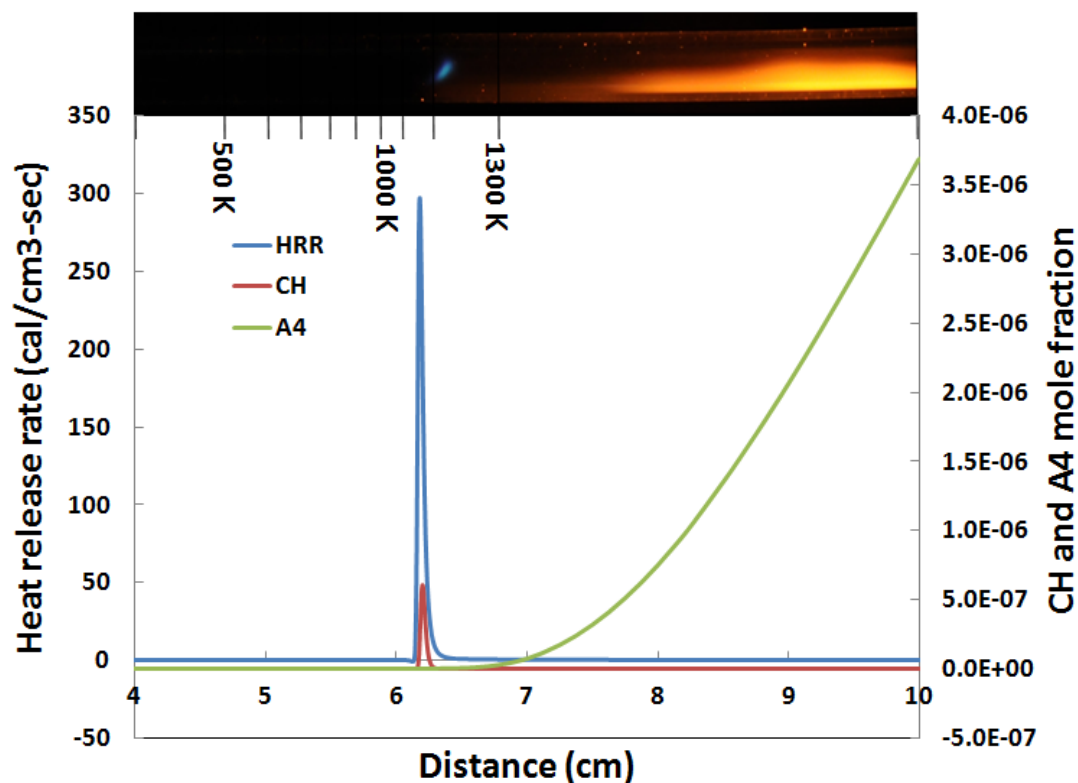


Figure 3. Direct flame image and comparison with computations for ethane flame ($\phi = 2$, $U_0 = 30$ cm/s).

Fig. 3 shows comparison of flame position with computed heat release and CH mole fraction peaks. Wall temperature shown at the top corresponds both to experiments and computations. The computations show reasonable agreement with experimental flame position. The experimental flame position is at 1212 K whereas computed heat release rate peak is at 1168.3 K and computed CH mole fraction peak is at 1175.5 K. Soot is formed after large PAHs coalesce and form a solid particle which

can then absorb molecules from gas phase to grow in size. So higher is the large PAHs mole fraction more will be the tendency of a flame to form soot. In the current work highest molecular weight PAH coronene had very low computed mole fraction. So A4 (Pyrene) is treated as higher PAH to represent sooting tendency. In Fig. 3 mole fraction of A4 is also shown. The flame image shows the formed soot as bright yellow luminosity region and this luminosity increases with distance. Soot is seen only at 1300 K for all experimental conditions. In the computations the mole fractions of higher PAHs are close to 10^{-6} or more only at 1300 K where soot is seen in experiments. The mole fraction of A4 thus starts increasing close to 1300 K and keeps increasing further until the end of reactor.

It should be noted that pyrene itself is not soot and pyrene was only used to explain the sooting tendency qualitatively for variations of equivalence ratio and mean inlet flow velocity.

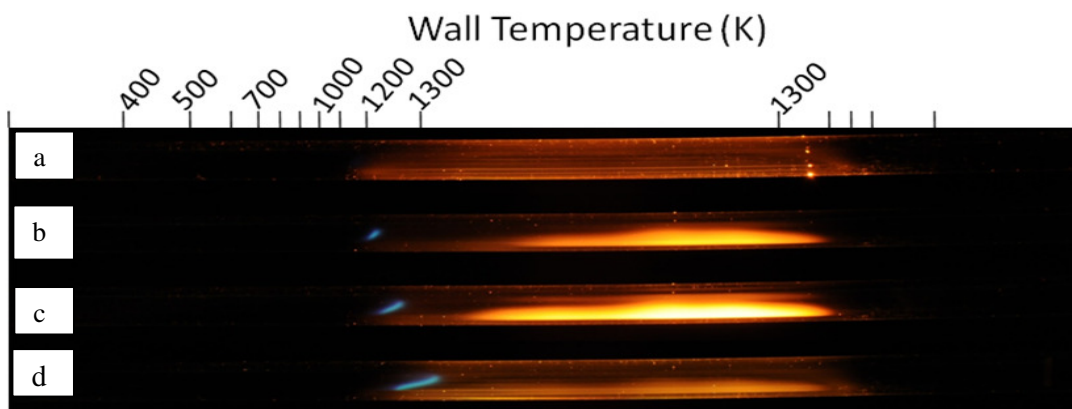


Figure 4. Flame and soot response of ethane at $\phi = 2$, (a) $U_0 = 10$ cm/s (b) 30 cm/s (c) 50 cm/s and (d) 80 cm/s.

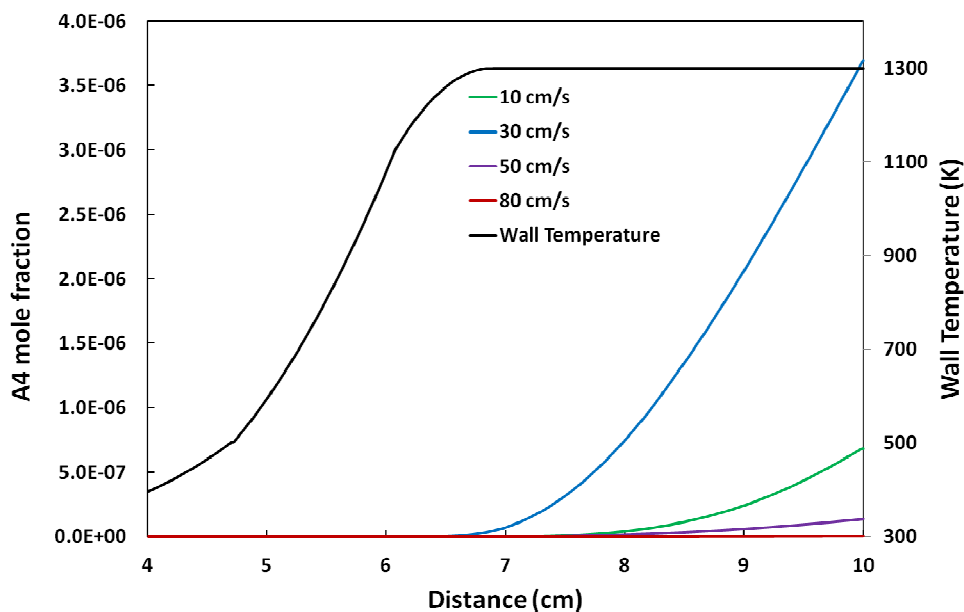


Figure 5. Computed A4 mole fraction for ethane flame at $\phi = 2$.

Fig. 4 shows flame and soot response for ethane at equivalence ratio 2 for different mean inlet velocity conditions. The amounts of soot or sooting region first increase with velocity, reach maxima and thereafter decrease. Fig. 5 shows computed mole fraction profiles for A4. Mole fraction profiles of A4 show similar tendencies to sooting region in experiments, i.e., first increase then decrease with increasing velocities. The inlet mean velocity at which maximum sooting occurs in the experiments (50 cm/s), though does not correspond to mean inlet velocity at which maximum mole fraction of A4 is seen in the computations (30 cm/s). At higher inlet velocity, mass flow through reactor is higher. So the number of active particles or nucleation sites can be higher which can assist in soot production. This is not the case in lower velocity region where mass flow is lower. Thus, even though A4 mole fraction is smaller soot production can still occur until mean inlet velocity becomes high enough. At high inlet velocity, residence time effects could take preference and soot production becomes less because there would not be enough time for soot production to effectively occur at that equivalence ratio.

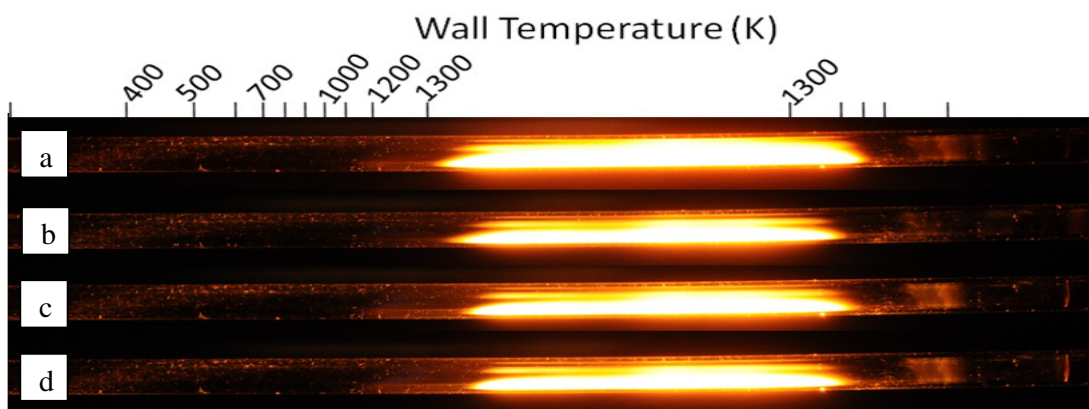


Figure 6. Flame and soot response of ethane at $\phi = 4$, (a) $U_0 = 10$ cm/s (b) 20 cm/s (c) 30 cm/s and (d) 40 cm/s.

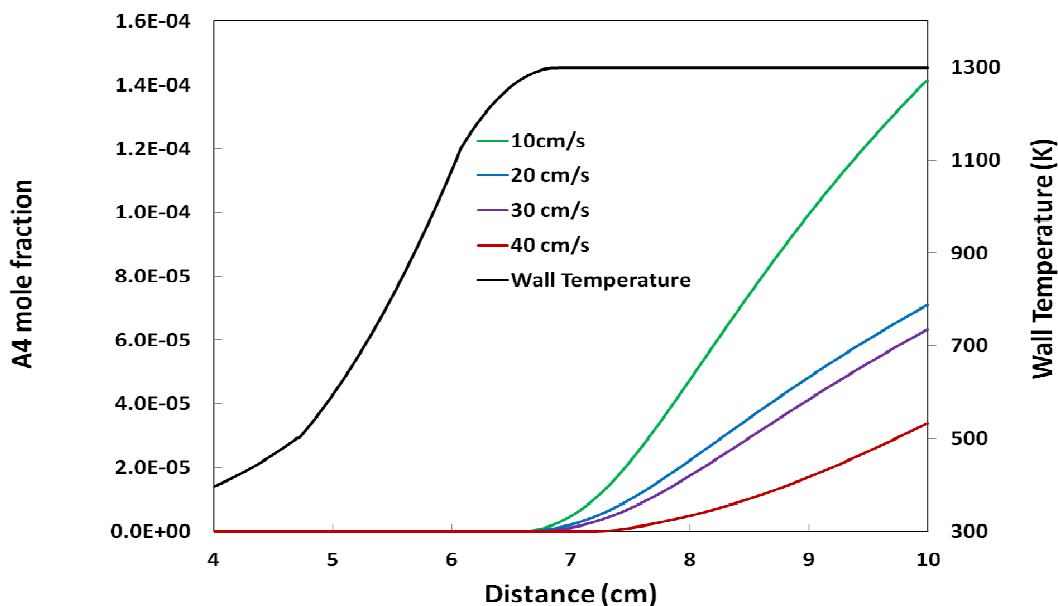


Figure 7. Computed A4 mole fraction for ethane flame at $\phi = 4$.

Fig. 6 shows soot and flame response for ethane at equivalence ratio 4 for different mean inlet velocities. Sooting region at equivalence ratio 4 is comparatively bigger than that at equivalence ratio of 2 due to higher amounts of PAHs formed. Also lengths of sooting region shorten slightly with increasing velocities which is unlike what is observed at lower equivalence ratio of 2. The computations shown in Fig. 4 successfully captured this tendency change with equivalence ratio. The maximum mole fractions of A4 are about 100 times higher at $\phi = 4$ compared to $\phi = 2$. The maximum A4 mole fraction decreases with the increase of mean inlet velocity in the computations.

5 Conclusions

In the current work sooting behavior of ethane was studied using a micro flow reactor with a controlled temperature profile. Three different kinds of “soot and flame” responses were observed for various equivalence ratio ($1.9 \leq \phi \leq 2.2$) and mean inlet flow velocity ($10 \text{ cm/s} \leq U_0 \leq 80 \text{ cm/s}$) conditions namely, flame, flame + soot and soot. Critical sooting equivalence ratio decreased with increasing mean inlet velocity. Soot is observed only in the flat-temperature region at 1300 K. Computed flame position showed good agreements with observed flame position. At equivalence ratio of 2, sooting region first increases then decreases with increasing mean inlet flow velocity whereas at equivalence ratio of 4, length of sooting region decreases slightly with increasing mean inlet velocity. Similar tendency was shown by computed A4 mole fractions.

Acknowledgements

The part of the study was supported financially by the Ministry of education and science of Russian Federation (project 14.Y26.31.0003). The authors express sincere thanks to Prof. Mani Sarathy & Mr. Muneeb Khurshid from KAUST for useful discussion.

References

- [1] Appel J, Bockhorn H, Frenklach M. (2000). Kinetic modeling of soot formation with detailed chemistry and physics: Laminar premixed flames of C_2 hydrocarbons. Comb. Flame 121(1-2): 122.
- [2] Melton TR, Inal F, Senkan SM. (2000). The effects of equivalence ratio on the formation of polycyclic aromatic hydrocarbons and soot in premixed ethane flames. Comb. Flame 121(4): 671.
- [3] Maruta K et al. (2005). Characteristics of combustion in a narrow channel with a temperature gradient. Proc. Combust. Inst. 30: 2429.
- [4] Nakamura H et al. (2014). Soot formation characteristics and PAH formation process in a micro flow reactor with a controlled temperature profile. Comb. Flame 161(2): 582.
- [5] Nakamura H et al. (2015). Sooting limits and PAH formation of n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane in a micro flow reactor with a controlled temperature profile. Proc. Combust. Inst. 35: 3397.
- [6] Wang Y, Raj A, Chung SH. (2013). A PAH growth mechanism and synergistic effect on PAH formation in counterflow diffusion flames. Comb. Flame 160(9): 1667.