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SOOTING PROPENSITY OF BINARY FUEL MIXTURES UNDER CONSTANT FLAME TEMPERATURE CONDITION[1]

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Introduction

Understanding pollutant emissions is an essential aspect of the study of combustion. The formation of soot, a primary contributor to airborne particulate matter (PM), has been increasingly scrutinized. The emission of fine particulate matter (PM) is a primary environmental concern and has been linked to serious health effects in humans and animals, adverse effects in plants, and environmental damage [1]. It is therefore crucial to gain better understanding of the complex phenomena leading to soot formation and by the same, gain insight on how to reduce these emissions.

Knowledge of the pathways to soot formation continues to evolve, however the complexity of the process is such that many uncertainties still remain. Although studying the sooting propensity of different elemental fuels has proven very useful in understanding these pathways, the advantages of looking at this process through a fuel mixture perspective are two-fold. First, in a theoretical aspect, it is generally agreed that studying the behaviour of mixtures of structurally different fuels can lead to better understanding of the actual formation process. Secondly, since a complete understanding seems unlikely at this point, the study of soot formation in binary fuel mixtures is an important approach towards understanding sooting characteristics of more complex and realistic multi-component fuels actually in use.

It is commonly agreed that the inception and growth stages of poly-aromatic hydrocarbons (PAH's) and soot involve acetylenic species. The reaction of acetylene with $n-C_4H_3$ and $n-C_4H_5$ was widely accepted as one of the more probable paths to the formation of the benzene aromatic ring. Some restrictions have however been introduced due to the tendency of $n-C_4H_3$ and $n-C_4H_5$ to convert to their more stable isomers $i-C_4H_3$ and $i-C_4H_5$ meaning that $n-C_4H_3$ and $n-C_4H_5$ would not be present in large enough quantities to account for the rate of aromatic formation [2]. This has led to the consideration of an additional path to the first ring formation through the propargyl (C_3H_3) recombination into either phenyl or benzene.

The analysis of fuel mixtures has further confirmed the importance of this path. Recent experiments that analyzed ethylene/propane mixtures [3] have found that for both co-flow and counter-flow ethylene/propane flames, the soot volume fraction and PAH concentrations were seen to be enhanced for certain mixture conditions, indicating the presence of a synergistic effect. Since adding propane to an ethylene mixture would tend to decrease the acetylene concentration, hence reducing the rate of first ring formation, a primarily acetylene based pathway would suggest a monotonic decrease in soot formation with increased propane fraction in the fuel mixture. However, the fact that a maximum soot and PAH concentration is reached for an intermediate mixture of ethylene and propane tends to confirm the importance of the propargyl combination reaction since propargyl is readily formed during the propane pyrolysis through the dehydrogenation process.

Numerical simulation of the gas phase species have confirmed that the C_2H_2 concentration monotonically decreases as the mixture fraction of propane is increased. However, the C_3H_3 concentration profile was seen to have a synergistic behavior similar to that of the soot and PAH concentrations. This indicates the possibility of a complementary behavior in the soot formation pathways between the acetylene and propargyl reactions. A similar, but less pronounced synergistic effect was seen in an ethylene/ethane flame [3]. As well, a recent study of a methane/ethylene mixtures in which the temperature was kept constant through nitrogen dilution indicated a synergistic effect in the soot concentration over the range of mixtures [4]. This was noticed as well in a methane doped n-heptane flame [5] providing additional evidence that methyl radicals can play an important role as well through reactions leading to propargyl.

This work aims at further exploring these phenomena. Firstly, the observations will be extended to other mixtures, namely methane/propane. As well, the experimental results will be correlated to numerical findings. The modeling will not be confined to gas phase species but will also attempt to directly observe the synergistic phenomena at the soot inception stage.

Experimental Set-up

Experiments were designed to offer a comparative basis to evaluate the sooting propensity of binary fuel mixtures by maintaining a constant carbon content in the fuel. This permits direct comparisons of the percent carbon conversion for all mixtures. For these experiments, the carbon flow rate was maintained at 3.23 mg/sec for all fuel mixtures which corresponds to flow conditions previously used by Gülder [6]. The mixtures were then combined to vary the relative contribution of each component to the total carbon in the fuel mixture. Three different sets of mixtures were studied: ethylene/propane, ethylene/methane and propane/methane. For all these mixtures, the contribution of each fuel component to the total carbon flow rate was varied from 0 to 100%. The Reynolds numbers of the pure fuels were 44, 45 and 58 for ethylene, methane and propane, corresponding to flow rates for the fuels of 194, 380 and 127 cc/min respectively.

In choosing the proper medium to evaluate the relative sooting propensity of binary fuel mixtures, a laminar co-flow diffusion flame was chosen. The burner used consisted of a 10.9 mm diameter brass fuel tube surrounded by a 100 mm diameter tube through which the co-flow air was delivered. The air flow rate was set at 284 LPM which created over ventilated diffusion flame conditions in all cases. To ensure a uniform velocity profile, this flow was passed through wire mesh screens and glass beads.

The soot inception of the different fuel mixtures was assessed using 2D line of sight attenuation (LOSA) [7]. This approach provides good accuracy, relatively fast measurements and good spatial resolution. The experimental technique used was as previously presented [8].

In order to properly compare the fuel mixtures, the percent carbon conversion was determined. To this effect, the soot volume fraction (f_v) was integrated radially as follows:

$$F_v(z) = \int_0^R 2\pi r f_v(r,z)dr$$

This value was multiplied by the velocity and the density as to obtain a mass flux of soot.

$$\dot{m}_{Soot} = \rho_s V_z F_v(z)$$

The density was taken as 1.9g/cm^3. The velocity was evaluated as follows:

$$V_z = \sqrt{2az}$$

Where z corresponds to the axial position in the flame and $a = 25 m/s^2$ [9]. This velocity assumes that the flame is buoyancy driven. This has been demonstrated to apply to both ethylene and methane flames [10,11] and is assumed in this case to also be applicable to propane flames. Although this buoyancy model is approximate in the lower part of the cooler methane flame, any discrepancy is minor since our focus is on the maximum mass flux of soot corresponding to a higher position in the flame. The percent carbon conversion or local soot yield (Ys) can be determined by taking the ratio of the local mass flux of soot at an axial position in the flame to the mass flux of carbon in the fuel as follows:

$$Y_s = \frac{\dot{m}_{soot}}{\dot{m}_{c\_fuel}}$$

The maximum local soot yield in each flame is a convenient measure by which to compare the maximum production of soot for different fuel mixtures.

Numerical Model

The model was based on the numerical scheme developed by Guo et al. [12]. However, some changes have been made to the chemical kinetics and soot sub-models. To account for the propane combustion, a new chemical kinetics model was used. The reaction model developed by Qin et al. [13] was chosen because it was optimized for the combustion of up to C_3 species. However, this model was found to over predict the soot volume fraction in propane flames and some reaction rates were adjusted accordingly.

The two equation soot model was based on that used by Guo et al. [14]. This soot model has the advantage of calculating the soot inception term based on the benzene and phenyl concentration. This accounts for all major pathways leading to first ring formation. The species phenyl was introduced to the inception model to account for the effect of hydrogen atom on PAH growth. The growth is modeled according to the hydrogen abstraction and acetylene addition reaction sequence (HACA) [15]. Although a constant value for the fraction of the available reactive surface (α) was used in [13], in this instance, the term was calculated using an equation which adds a dependence on temperature similarly to the term presented by Appel et al. [15].

Results and Discussion

Experiments were conducted to assess the presence of a synergistic effect in binary fuel mixtures and to relate sooting propensity to chemical kinetic processes. A synergistic effect had been reported by Hwang et al. in an ethylene/propane mixture [3]. The synergistic effect actually refers to the presence of a non-cumulative sooting propensity, where, in the ethylene/propane mixture for example, adding a small amount of propane induces a dramatic increase in the soot yield. An initial goal was to reproduce and confirm these phenomena under different flow and burner conditions from the previously reported experiment. As shown in Figure 1, a synergistic effect was observed considering both the peak soot volume fraction and the peak percent carbon conversion and was shown to be reproducible.
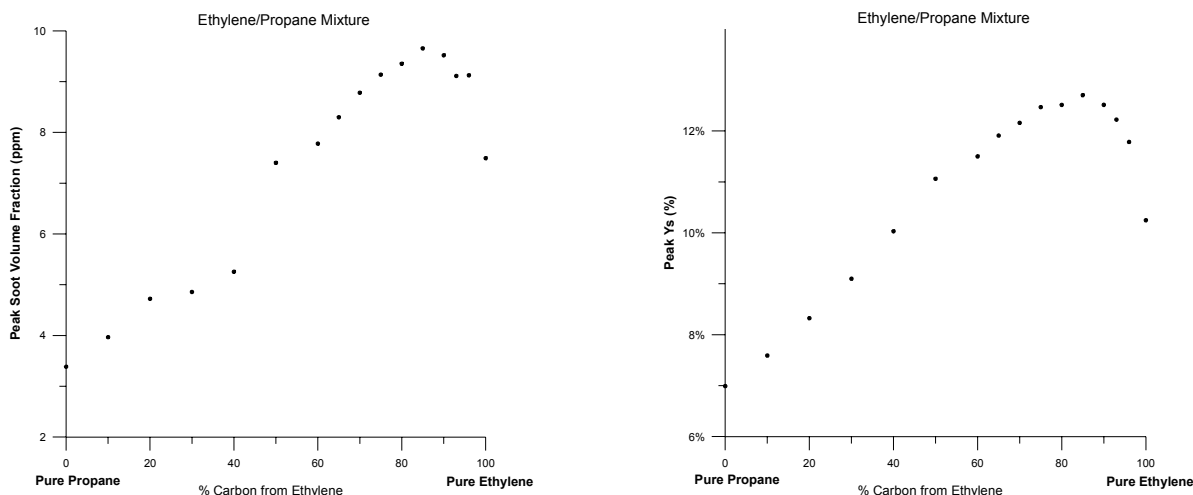
Figure 1 Ethylene/Propane Mixture

The synergistic effect peaks at a mixture where 85% of the carbon in the fuel comes from ethylene. This is accordance with the findings of Hwang et al. The peak soot volume fraction at this mixture was 9.7 ppm, corresponding to a 29% increase from the peak soot volume fraction for a pure ethylene flame which was 7.5 ppm.

The ethylene/methane mixture did not exhibit such a strong effect. However, the synergy is apparent when the deviation of percent carbon conversion from a purely linear trend is examined, as in Figure 2. The previously reported synergistic effect was measured under constant temperature condition [4]. Considering that in the present experiments the adiabatic flame temperature of the fuels naturally varies by 150 K, it is thought that the actual synergistic effect has been obscured by the concurrent effect of changing flame temperature with varied mixture composition. This highlights the need to eliminate this variable from the experiments as to isolate the chemical kinetics effect.

No indication of a synergistic effect was experimentally observed for propane/methane flames as shown in Figure 3. Since the total variation in the adiabatic flame temperature is only 50 K, this suggests that a synergistic effect is not being obscured and is unlikely to exist even if the flame temperature is maintained constant over the mixture range.

From these observations, key information can be obtained as to the pathways to soot formation in these fuels. The synergistic effect measured in both the ethylene/methane and ethylene/propane flames can not be explained if only the acetylene based pathway to soot formation is considered. Since one could expect the acetylene concentration to decrease linearly as the contribution of propane or methane is increased, the soot concentration should follow the same linear trend if the acetylene pathway is dominant. However, the presence of an actual synergistic effect indicates the importance of a second pathway, which is most probably based on the propargyl recombination. The synergistic effect would therefore be an interaction of these two phenomena.

In the methane/propane experiments, the linearly decreasing soot concentration suggests the absence of any interaction or competing reactions. This indicates that for both propane and methane, the dominating pathway to soot formation would be the same.
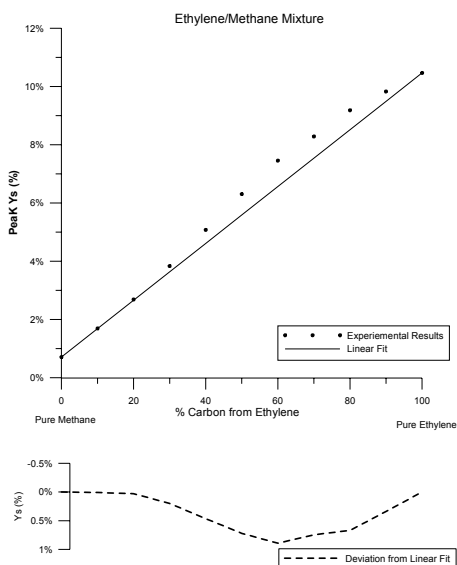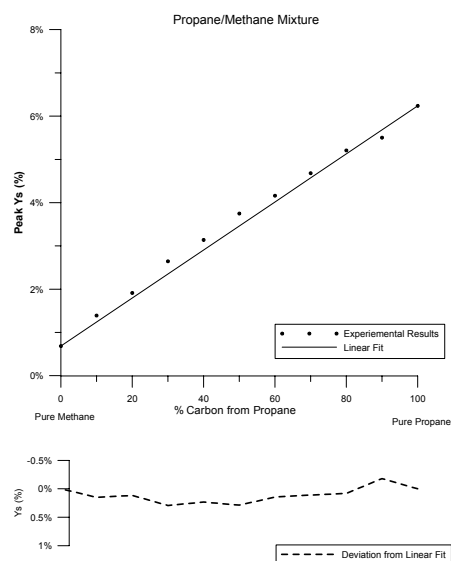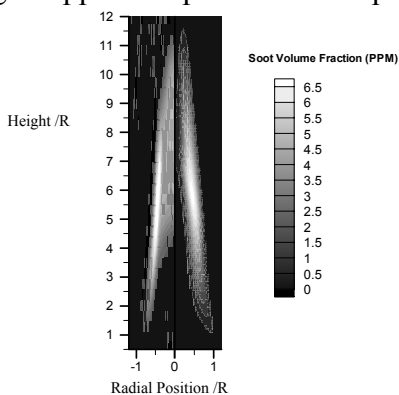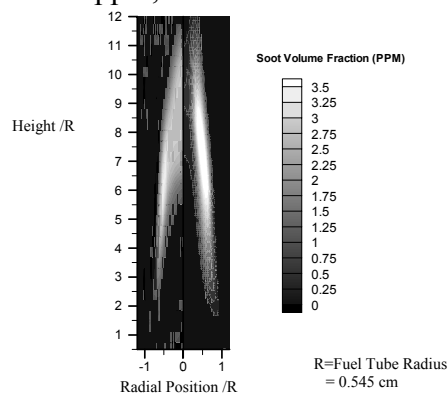
Figure 2 Ethylene/Methane Mixture

Figure 3 Propane/Methane Mixture

As shown in Figures 4 and 5, the model yielded very reasonable results for both the pure ethylene and pure propane flames. Specifically, the flame height and location of maximum soot volume fraction agreed very well with experimental values. The modeled ethylene flame yielded a maximum soot volume of 6.85 ppm, a value 9% smaller than the experimental value of 7.5 ppm. The maximum soot volume fraction for propane was slightly over predicted by the model, yielding 4.8 ppm compared to the experimental value of 3.6 ppm, an increase of 33%.

Experimental VS Numerical Results

Figure 4 Ethylene Flame

Experimental VS Numerical Results

Figure 5 Propane Flame

The ethylene/propane mixture was also modeled in an effort to reproduce the observed synergistic effect. It was found that the effect was numerically reproducible in a qualitative sense and could be correlated directly to the increase in propargyl concentration and the decrease in acetylene concentration. However, whereas the experimental effect resulted in an increase of 29 % for the peak soot volume fraction, the model predicted an increase of only 4%. As well, this increase was seen to peak at a mixture where the carbon contribution from ethylene was 96%, compared to 85% for experimental. The propargyl concentration was seen to increase with increased propane contribution, leading to an increase in benzene concentration. As propane was substituted for ethylene in the fuel, the phenyl concentration was seen to initially decrease due to a rapid diminution of the acetylenic reaction rate. The phenyl concentration subsequently increased as the propargyl combination reaction gained in importance. This behavior raises

questions as to the inception model which is directly dependent on the benzene and phenyl concentrations. It was found that the phenyl concentration trend had an exaggerated effect on the inception rate. It is therefore concluded that the soot inception and growth model need to be further refined before any conclusions can be drawn as to the causes of the synergistic effect.

To further assess the importance of the temperature time history variation on the sooting propensity of a fuel, a propane flame was simulated where the temperature profile of the flame that of an ethylene flame. In the numerical model, the temperature variation between both fuels was 85 K. It was found that the peak soot volume fraction of the flame increased to 7.5 ppm, an increase of 50% from the soot yield of the propane flame at its original temperature. Although the soot volume fraction for the ethylene flame was found to be 6.85 ppm, it needs to be stressed here that this does not reflect a superior sooting tendency of propane under similar temperature conditions since the model is known to over predict the sooting tendency of this fuel.

Both these numerical and experimental results highlight the importance of the temperature variation between flames on the sooting propensity, and impose the necessity of evaluating these phenomena under constant flame temperature simply to uncover the pure chemical kinetics effects. Experiments are currently being planned to assess sooting propensity while maintaining constant flame temperatures.

Conclusion

A synergistic effect in the sooting propensity for both ethylene/propane and ethylene/methane fuel mixtures was observed experimentally. However for a propane/methane mixture, no synergistic effect was noticeable. This confirms the probable cause of this effect as being an interaction between acetylenic and propargyl based pathways to soot formation.

This effect was also qualitatively reproduced numerically; however, some improvements would need to be done to both the soot inception and soot growth models to obtain a more detailed insight into the most relevant reactions.

Finally, both numerical and experimental results have highlighted the necessity in pursuing these measurements under constant flame temperature conditions.

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