HEFAT2007
5th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics
Sun City, South Africa
Paper number: MA1

COMPARISON OF SYNERGISTIC EFFECT OF ETHYLENE-PROPANE AND ETHYLENE-DME ON SOOT FORMATION OF ETHYLENE-AIR FLAME

M. Mbarawa[1*], W. Lee[2], Y.W.Nam[2] and S.H.Chung[3]
[*1]Department of Mechanical Engineering, Tshwane University of Technology, Pretoria 0001, South Africa
Tel. +27 12 382 5177, Fax +27 12 382 5062; Email: mbarawamm@tut.ac.za
[2]Department of Mechanical Engineering, Dankook University, Seoul 140-714, Korea
[3]Department of Mechanical Engineering, Seoul National University, Seoul 140-742, Korea
E-mail: mbarawamm@tut.ac.za

ABSTRACT

In this study, the synergistic effects of ethylene-propane and ethylene-dimethyl ester (DME) mixtures on soot formation were investigated experimentally using a co-flow diffusion flame burner. The soot volume fraction, soot particle diameter, and number density were measured and compared to the homogenous mixture. Addition of DME and propane to the ethylene fuel increased soot volume fraction in the ethylene flames. The ethylene-propane has more pronounced synergistic effect in comparison to the ethylene–DME flames. This is due to the fact that during the decomposition of propane some methyl radicals are generated. The reactions related to these methyl radicals promote the formation of propargyl radicals consequently the formation of benzene through propargyl self-reaction and finally to the soot formation. Although DME decomposition produces methyl, C-O bond in the DME removes some carbon from the reaction path to form soot. Hence the soot formation in ethylene-DME mixture is much lower than that of ethylene-propane mixture.

INTRODUCTION

Soot formation and emission are dominant features of hydrocarbon–air diffusion combustion equipment such as internal combustion engines, gas turbines, and industrial furnaces. Soot emission from any combustion equipment reflects poor combustion and loss of efficiency. Furthermore, soot is a major pollutant and raises health concerns related to inhalation of soot particles. As a result, it is important to gain a fundamental understanding of complex soot formation processes in flames and their control mechanisms.

The effect of fuel structure on the formation of polycyclic aromatic hydrocarbon (PAH) and soot has been emphasized in diffusion flames [1-5], since radicals influencing the formation and growth, such as acetylene (C_2H_2) and propargyl (C_3H_3), are affected by fuel structure and its pyrolysis characteristics. The species generated from fuel pyrolysis lead to incipient ring formation such as benzene (C_6H_6) and naphthalene ($C_{10}H_8$), which grow to PAHs and finally to soot [6-9].

It has been shown that the mixing of ethylene and propane considerably enhances the formations of PAHs and soot as compared to those with respective pure fuels [1]. This enhancement has been explained based on the interaction between acetylene and propargyl species. Acetylene has been known to be an important species for the hydrogen-abstraction-C_2H_2-addition (HACA) mechanism and propargyl for both the benzene ring formation through the propargyl recombination reaction and PAH growth through odd-carbon chemistries [10–12]. The mixing of propane in ethylene fuel could enhance the production of soot and PAHs by providing extra propargyl radicals from the dehydrogenation of propane, together with the abundant acetylene.

Recently, it has been observed that the addition of dimethyl ester (DME: CH_3OCH_3) in ethylene fuels in coflow diffusion flames increased the maximum soot volume fraction in the ethylene flames, even though ethylene is a much sootier fuel than DME [13]. The detailed species measurements by McEnally & Pfefferle [13], suggest that the DME increases soot concentrations because it decomposes to methyl radical, which promotes the formation of propargyl radical (C_3H_3) through C1

NOMENCLATURE

d	[nm]	soot particle diameter
f		soot volume fraction
DME		dimethyl ester
HACA		hydrogen-abstraction-C_2H_2-addition
i.d	(mm)	internal diameter
LS/E		laser-light extinction
N	[*(#/cm^3)*]	total number density of soot particles per unit volume
PAH		polycyclic aromatic hydrocarbon
Z	(cm)	height above the burner exit
Subscript		
p		particle
v		volume

+ C2 addition reactions and consequently the formation of benzene through propargyl self-reaction.

The present study aims to provide better insight into the synergistic effect of propane and DME addition on soot formation of ethylene-air flames.

EXPERIMENTAL METHOD

General apparatus

The investigation of the synergistic effects on soot formation was carried out in the co-flow ethylene-air diffusion flames. The co-flow burner is of a standard type and consists of an inner brass fuel tube (i.d. 8 mm) for fuel supply surrounded by an outer brass tube (i.d. 80 mm) for the air flow. The fuel passage contains screens and 3 mm glass beads to provide a uniform exit flow profile. The larger air passage also utilizes a series of screens with a section filled of 3.0 mm glass beads. A ceramic honeycomb section is used as the final section of the air-flow passage for flow stabilization and uniformity in the outer tube. The fuel tube extends 4 mm beyond the exit plane of the outer tube. The flow conditions chosen for these studies always result in an over-ventilated diffusion flame. The fuel used was commercially pure grade ethylene (>99.9%). The oxidizer was 76% N_2/24% O_2. Two fuels (propane (C_3H_8) and DME) were selected to compare the synergistic effect on the soot formation of ethylene-air flames. Propane was selected because its synergistic effects on ethylene-air flames are well known [1]. The propane results will provide a point of comparison for the synergistic effects of DME. DME was selected because it has been the subject of numerous combustion studies and has been investigated in diesel engines as an additive to reduce soot. DME has no carbon-carbon (C-C) bond; the absence of C-C bound is believed to be responsible for the extremely low soot emissions from engines fuelled with DME. Ethylene (C_2H_4) was chosen as the base fuel because first, it has a much higher propensity to soot, which makes it relatively easy to utilize optical diagnostic equipment; second, C_2H_4 has been widely used in studies of soot formation for many years, so a large database exists upon which comparison can be made.

For current experiments, small amounts of propane (14%) and DME (15%) were added to the fuel side of the ethylene diffusion flames, while the total carbon flow rate has been kept constant for each flame. These values of addition were selected because the measurements by two of the authors (Lee, Nam) in diffusion DME-air flames have shown that the 15% DME has strong synergistic effects, while study by Hwang et. al [1] showed that the 14% propane in ethylene-air flames has significant synergistic effects.

Basic flow rates for the experiments were 180 mL/min and 60 L/min for ethylene and air respectively. These values were chosen because they gave the most stable flame. The flow rates of fuels and air were measured using flow control system consisting of mass-flow controllers and calibrated mass-flow meters.

Laser scattering and extinction optics

A standard laser-light extinction technique was employed to measure the soot volume fraction distributions, soot particle diameter and number density of soot particles within the tested flames. Figure 1 shows the optical arrangement for the laser scattering and extinction measurements. An Argon-ion laser (Spectra- Physics Stabilite 2017-05) emitting vertically polarized light at a wavelength (λ) of 514.5 nm was used as a light source. The laser power was set to either 1 W for laser scattering tests or 0.5 W for laser extinction tests. The laser beam was first chopped at 1 kHz with a mechanical chopper. Then, it was focused to a beam waist of 0.3 mm at the burner center with a 500-mm-focal-length lens. The optics for collecting scattering signal consisted of an optical fiber module, polarizer, circular aperture collection lens, pin-hole aperture and laser line filter of 514.5 nm. Neutral density filters were used to reduce the scattered light intensity when it was required. The scattering signal optics was placed at 90^o to the laser beam. The scattering signal from the optical fiber module was measured with a lock-in amplifier (Spectra- Physics Stabilite; SR830). The output signals from the lock-in amplifier were transferred to a computer via a data-acquisition system using the Labview program for storage and subsequent data analysis. For each test location, 5000 data points were collected over 5 s to measure time-averaged scattering coefficients with less than 10% experimental uncertainties. This gives uncertainties for soot volume fraction and soot primary particle diameter at 95% confidence interval of about ± 5% of the mean values.

Before the experiments were performed, the scattered light detection systems were calibrated to account for the effects of the incident laser power, sample volume, light collection efficiency, optical fiber module sensitivity and electronic gain of the system. The calibration was accomplished by passing C_2H_4, which has a known Rayleigh scattering cross-section through the fuel passage of the burner and measuring the resulting scattered light intensities. For checking the optical alignment and verifying the operation of the entire optical setup, the scattered light detection systems were calibrated by

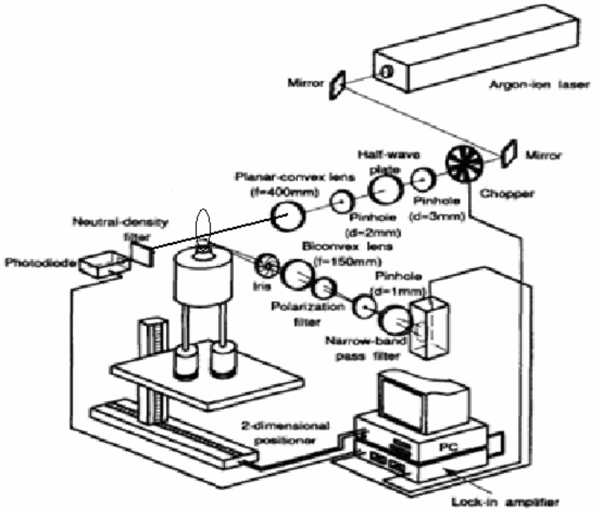

Figure 1. Extinction/scattering experimental set-up.

using nitrogen. Nitrogen was separately supplied to the burner to measure the scattering signals under the exact conditions of the actual flame experiments.

RESULTS AND DISCUSSIONS

Luminous Flame Appearance

Figure 2 presents the digital pictures of the pure C_2H_4–air flame, the (14% C_3H_8 + 86% C_2H_4)-air flame and (15% DME + 85% C_2H_4)-air flame under the same conditions. The images of all flames were taken at the same exposure time. At the chosen flow rate, the C_2H_4–air flame burns slightly under the smoke point height, while the (14% C_3H_8 + 86% C_2H_4)-air flame and (15% DME + 85% C_2H_4)-air flame at the same fuel flow rate burn above their smoke point and soot escapes from the tip of the flames. The flame heights were 77mm, 74 mm and 73mm for the (14% C_3H_8 + 86% C_2H_4)-air flame, (15% DME + 85% C_2H_4)-air flame and the C_2H_4–air flame respectively. The luminosity of the flame reflects the radiation from soot particles, and the more soot in the flame, the brighter the flame. From the figure can be seen that the (14% C_3H_8 + 86% C_2H_4)-air flame are generally brighter than those of C_2H_4-air flame and the (15% DME + 85% C_2H_4)-air flame. It can also be seen that there is a gap between burner surface and the luminous region of the flame, which indicates that there is no soot at the location near burner surface, and the soot begins to appear after that.

Pure C_2H_4 14%C_3H_8 +86% C_2H_4 15% DME + 85%C_2H_4

Figure 2 Digital images of diffusion flames

The synergistic effect of the ethylene-propane mixture on soot formation was investigated. Figure 3 shows the variation in integrated soot volume fraction obtained by integrating the soot volume fraction with respect to radius, versus the distance *(z)* above the burner exit, when propane is added to ethylene at various propane ratios. In this set of experiments, the outer air velocity and the total carbon flow rate were maintained at 20.0 cm/s and 0.193 g/min, respectively. Here, the propane ratio χ is defined as $\chi = Q_{prop} / Q_{tot}$, where Q_{prop} is the volumetric flow rate of propane and Q_{tot} is the total volumetric flow rate of ethylene and propane. Soot volume fraction increases initially with height, attains a peak value, then decreases with axial distance and eventually vanishes near the tip of the flame. The results show that the maximum soot volume fraction varies nonmonotonically with χ such that the synergistic effects are exhibited. For example, the maximum soot volume fraction for $\chi = 0.14$ are larger than the corresponding maximum value for $\chi = 0.0$ or 1.0. The peak value of the maximum integrated soot volume fraction, occurs at $\chi = 0.14$, as shown in Figure 4. Nonlinear synergistic effects of ethylene–propane mixture on soot formation are clearly demonstrated.

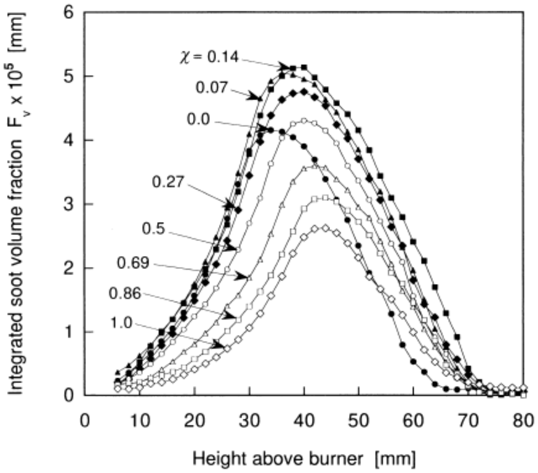

Figure 3 Axial profiles of integrated soot volume fraction in co-flow diffusion flames for various ethylene–propane mixtures [1]

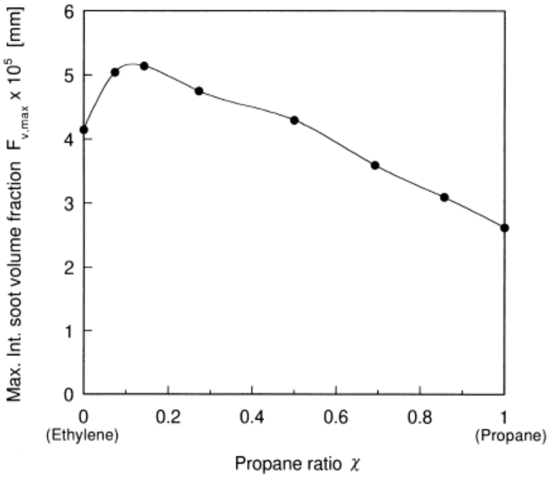

Figure 4 Maximum integrated soot volume fraction as a function of propane ratio in co-flow diffusion flames [1]

Figure 5 shows the integrated soot volume fractions versus the distance *(z)* above the burner exit for the C_2H_4-air flame, the (14% C_3H_8+86% C_2H_4)-air flame, the (15% DME+85% C_2H_4)-air flame under similar conditions. The integrated soot volume fraction increases initially with height attains a peak value in the flame, and thereafter decreases along the flame height. This trend is observed for all flames. The figure shows that the addition of either propane or DME to the fuel enhances the formation of soot in the ethylene–air diffusion flame. However, although the fraction of added propane (14%) is lower than that of added DME (15%), the enhancement of soot volume fraction due to the addition of propane is more significant. This synergistic effect of propane in soot formations has been attributed to the competition between the incipient ring formation and the subsequent growths of PAH and soot [5]. For example, the formation of a benzene ring from the propargyl recombination can be more effective for propane-rich flames, since propargyl can maintain relatively high concentrations with the addition of propane through dehydrogenation reactions [1, 2]. Consequently, the production of PAHs can be enhanced by the abundance of incipient rings. Meanwhile the concentration of acetylene and the adiabatic flame temperature will be higher in ethylene-rich flames. Thus, the growths of PAHs and soot through the temperature-sensitive HACA pathways will be more pronounced. It has been reasoned that the synergistic effect occurs for propane mixture fuels by the interaction between the incipient benzene ring formation from propargyl recombination and the PAH and soot growth through the HACA pathways [5]. On the other hand, the dissociation of DME undergoes hydrogen abstraction followed by bond scission, leading to the formation of methyl and formaldehyde (CH_2O). Formaldehyde is entirely converted into HCO by hydrogen abstraction through. HCO is finally converted into CO through hydrogen abstraction reactions. Due to the strength of the C=O bond, CO will not contribute to the production of aromatic species so any carbon from the DME that produces CO is considered to be removed from the reaction pathway leading to aromatic species and soot. Therefore, the carbon in CH_2O does not contribute to PAH formation and soot growth, and thus 50% of the carbon in DME makes no contribution to soot formation. Though the other 50% of the carbon in DME is converted into CH_3, most CH_3 makes no contribution to PAH formation. This could be due to the active nature of CH_3 radicals. The methyl production/recombination routes convert approximately 30% of the carbon that makes potential contribution to PAH and soot growth [14]. Unlike propane addition, where the synergistic effects produced by the competition between the incipient ring formation and the subsequent growths of PAH and soot, for DME, it comes mainly from the methyl via propargyl radical (C_3H_3) through C1 + C2 addition reactions and consequently the formation of benzene through propargyl self-reaction. As can be seen in the figure, the addition of DME to ethylene diffusion flame has modest synergistic effects.

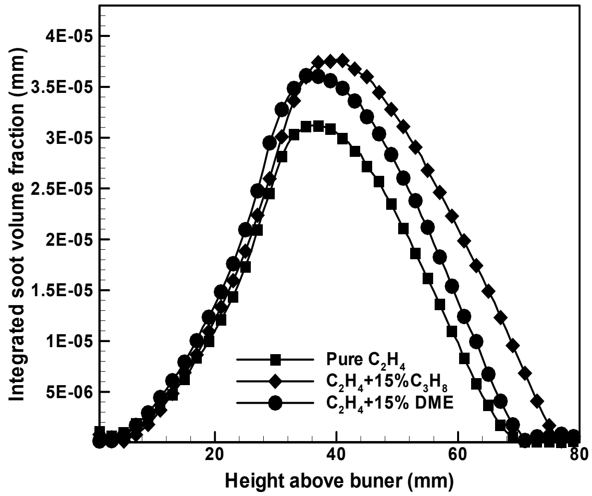

Figure 5 Axial profiles of integrated soot volume fraction for three different flames

Figures 6a-c display the radial variations of the soot volume fraction for the C_2H_4-air flame, the (14% C_3H_8+86% C_2H_4)-air flame, and the (15% DME+85% C_2H_4)-air flame at different heights above the burner exit. The eight axial locations were chosen to demonstrate the representative regions of soot inception *(z = 10mm and 15mm)*, surface growth (*z = 20mm to 40mm)* and oxidation region *(z = 45 mm)*. The data presented in the figures was only half of the flame width due to the axisymmetric conditions of the flames. At lower locations, the peak radial soot volume fraction occurring primarily in the outer flame regions. This trend disappeared at the higher locations, whereby the soot volume fractions occurred at about 2-3 mm from the flame centreline. This trend is observed for all flames. In the case of the C_2H_4-air flame, the overall maximum soot volume fraction through the entire flame was ~10.767 ppm and was measured at *z =35* mm (see Fig. 6a).

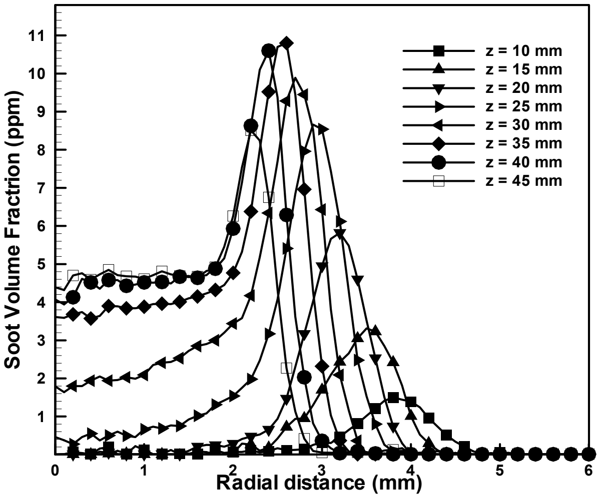

Figure 6a Radial profiles of soot volume fraction for the pure C_2H_4–air flames

Figure 6b presents the radial distributions of the soot volume fractions in the (14% C_3H_8 + 86% C_2H_4)-air flame. The maximum soot volume fraction of approximately *16* ppm was measured at *z* = 40 mm above the burner.

Figure 6c shows the radial distributions of the soot volume fractions in the (15% DME+85% C_2H_4)–air flame at different axial locations. The overall maximum soot volume fraction through the entire flame appears to be approximately *13.5* ppm and was measured at *z =35* mm. Compare these three cases, the (14% C_3H_8+ 86% C_2H_4)-air flame displays a strong synergistic effects than the (15% DME + 85% C_2H_4)-air flame. As mentioned earlier the synergistic effects of the propane are due to the competition between the incipient ring formation and the subsequent growths of PAH and soot [1, 2]. DME has moderate synergistic effect because only about 30% of its carbon contributes to PAH and soot growth [14].

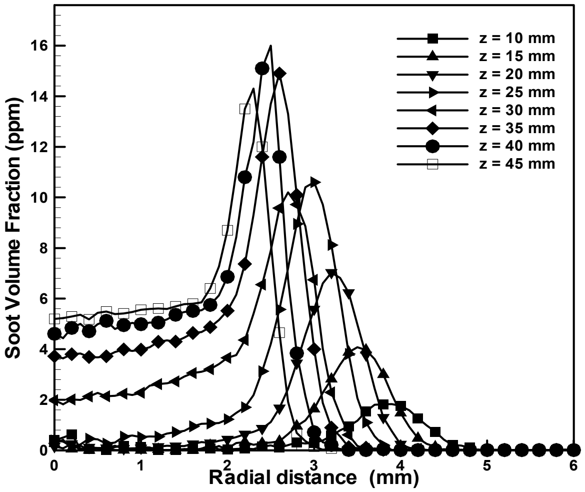

Figure 6b Radial profiles of soot volume fraction for the (14% C_3H_8 + 86% C_2H_4-air) flame

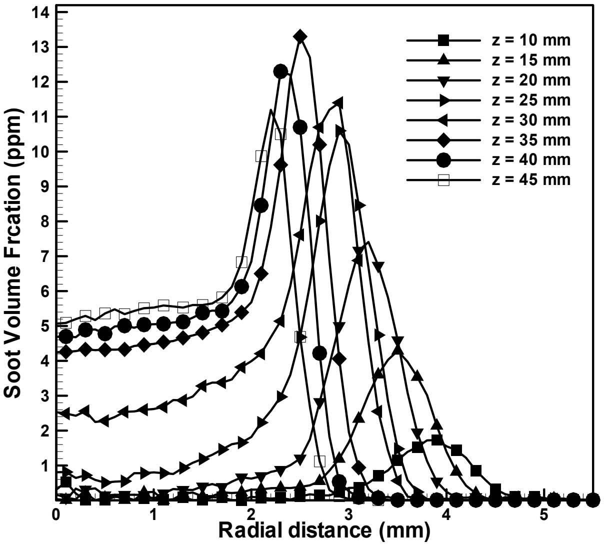

Figure 6c Radial profiles of soot volume fraction for the (15% DME+ 85% C_2H_4-air) flame

Table 1 lists the overall maximum soot primary diameter ($d_{p,max}$), along with the specific axial locations (Z) where these values were measured in the tested flames. The table also lists the measured values of soot volume fraction (f_v) at the ($d_{p,max}$) values as well as the calculated number density of soot particles per unit volume (N_p).

$$N_p = \frac{6fv}{\pi d_p^3} \qquad (1)$$

where, $f_{v\ p}$ are soot volume fraction and soot particle diameter respectively.

As seen in the table, $d_{p,max}$ at z = 20 mm above the burner exit for the (14% C_3H_8 +86% C_2H_4)-air flame is ~18.2% and 6.45% higher than that for the C_2H_4-air flame and the (15% DME+85% C_2H_4)-air flame respectively. The higher $d_{p,max}$ of the (14% C_3H_8 +86% C_2H_4)-air flame is accompanied with a lower N_p value. These results suggest that the higher amount of soot volume fraction for the (14% C_3H_8 +86% C_2H_4)-air flame case is caused by the growth of the soot particles due to the condensation of growth species, C_2H_2 and/or PAH on the soot particle surface. In the case of the (15% DME+85% C_2H_4)-air flame and the C_2H_4-air flame, the lower amount of the soot volume fraction and higher N_p values observed are due to nucleation process and slower particle size growth rates after particles are incepted. However, it should be noted that the contribution of nucleation to total soot is not significant in diffusion flame. At z = 30 mm, for all tested flames, the dominance of surface growth rate is apparent from the increasing of $d_{p,max}$ and decreasing of the N_p value. At this location, $d_{p,max}$ of the (15% DME +85% C_2H_4)-air flame becomes higher than the (14% C_3H_8 +86% C_2H_4)-air flame and C_2H_4-air flame by 2.4% and 25.5% respectively. At the upper location (z = 40 mm), $d_{p,max}$ for the (14% C_3H_8 +86% C_2H_4)-air flame increases, while N_p value continuously decreases. On the other hand, for the (15% DME +85% C_2H_4)-air flame and C_2H_4-air flame, $d_{p,max}$ values decrease, while N_p values continuously increase. The shrinking of $d_{p,max}$ for (15% DME +85% C_2H_4)-air flame and C_2H_4-air flame means the beginning of the oxidation process. Thus soot oxidation process for these two cases starts earlier. In these flames, soot formation and oxidation processes proceed at the same time, with the soot formation being dominant up to the maximum soot volume fraction location, and soot oxidation dominating the process thereafter. The relationship between soot concentration and primary soot particle size, however, is complex due to a varying degree of soot nucleation, growth and oxidation rates.The soot growth rates stronger with the (14% C_3H_8 +86% C_2H_4)-air flame than the (DME +85% C_2H_4)-air flame. Thus the synergistic effect is more pronounced in ethylene–propane diffusion flames and less pronounced in ethylene–propane diffusion flames.

Table1 Selected soot aerosol properties in the three tested flames

Flame	*Z (mm)*	$d_{p,max}$ *(nm)*	*fv (ppm)*	N_p (#/cm^3)
Pure C_2H_4	20	67	5.8	1169×10^9
86% C_2H_4+ 14% C_3H_8	20	75	7.0	1009×10^{10}
85% C_2H_4+ 15% DME	20	71	7.2	1182×10^9
Pure C_2H_4	30	110	9.9	440×10^9
86% C_2H_4+ 14% C_3H_8	30	135	10.2	249×10^9
85% C_2H_4+ 15% DME	30	130	11.4	314×10^8
Pure C_2H_4	40	106	10.6	542×10^9
86% C_2H_4+ 14% C_3H_8	40	140	16	353×10^9
85% C_2H_4+ 15% DME	40	119	12.30	436×10^8

CONCLUSION

The synergistic effect of ethylene-propane and ethylene-DME mixtures on soot formation has been studied in axisymmetric co-flowing acetylene–air laminar diffusion flames using the laser light-extinction technique. The (14% C_3H_8 +86% C_2H_4)-air flame, the (DME +85% C_2H_4)-air flame and C_2H_4-air flame were studied and results on soot volume fraction, primary particle diameter, and particle number density were compared. The main findings from this study are as follows:

- Soot volume fractions in the ethylene–propane and ethylene-DME mixture flames are higher than those of the pure ethylene flames. Ethylene–propane mixture produced a larger increase in soot than the ethylene-DME mixture flame.
- At lower location, $d_{p,max}$ for the (14% C_3H_8 +86% C_2H_4)-air flame was ~18.2% and 6.45% higher than that for the C_2H_4-air flame and the (15% DME+85% C_2H_4)-air flame respectively;
- At middle location, $d_{p,max}$ of the (15% DME+85% C_2H_4)-air flame becomes higher than the (14% C_3H_8 +86% C_2H_4)-air flame and C_2H_4-air flame by 2.4% and 25.5% respectively.
- At the upper location, $d_{p,max}$ for the (14% C_3H_8 +86% C_2H_4)-air flame increases, while N_p value continuously decreases. On the other hand, for the (15% DME +85% C_2H_4)-air flame and C_2H_4-air flame, $d_{p,max}$ values decrease, while N_p values continuously increase.
- The synergistic effect is more pronounced in the ethylene–propane diffusion flames and less pronounced in the ethylene-DME diffusion flames.

REFERENCES

[1] Hwang, J. Y., Chung, S.H., Kang, H.G and Lee, W., Synergistic Effect of Ethylene-Propane Mixture on Soot Formation in Laminar Diffusion Flames, *Combustion and Flame*, Vol. 191, (1997), pp 427-434.

[2] Hwang, J.Y., Chung, S.H. Lee, W. P *Twenty-Seven* Symposium *(International) on Combustion, The Combustion Institute, Pittsburgh,* Vol. (27), (1998) 1531–1538.

[3] Vandsburger, U., Kennedy, I., and Glassman, I., Sooting counterflow diffusion flames with varying oxygen index, *Combustion Science and Technology*, Vol. 39, (1984) pp 263–285.

[4] Gomez, A. and Glassman. I., Quantitative Comparison OF Fuel Soot Formation Rates in Laminar Diffusion Flammes, *Twenty-First* Symposium *(International) on Combustion, The Combustion Institute, Pittsburgh,* 1968, 1087.

[5] Hura, H.S. and Glassman, *Combustion Science and Technology*. 53 (1987) 1–21.

[6] M. Frenklach, D.W. Clary, C. William, J.R. Gardiner, E.S. Stephen, Proc. Combust. Inst. 20 (1984) 887– 901.

[7] H. Wang, M. Frenklach, Combust. Flame 110 (1997) 173–221.

[8] Frenklach, M. and Wang, H., Detailed modeling of soot particle nucleation and growth*, Twenty-Third* Symposium *(International) on Combustion, The Combustion Institute, Pittsburgh,* Vol. (23), (1991) 1559–1566.

[9] M. Frenklach, *Twenty-Third* Symposium *(International) on Combustion, The Combustion Institute, Pittsburgh,* Vol. (26), (1996) 2285– 2293.

[10] A. DAnna, A. Violi, Proc. Combust. Inst. 27 (1998) 425–433.

[11] Miller, J.A. and Melius, C.F.**,** Kinetic and thermodynamic issues in the formation of aromatic compounds in flames of aliphatic fuels Combust. Flame 91 (1992) 21–39.

[12] Marinov, N.M., Pitz, W.J., Westbrook, C.K., Castaldi, M.J., and Senkan, S.M., Modeling of Aromatic and Polycyclic Aromatic Hydrocarbon Formation in Premixed Methane and Ethane Flames, *Combustion Science and Technology,* pp 34-42, 1996.

[13] McEnally, C.S., and Pfefferle, L.D., The effects of dimethyl ether and ethanol on benzene and soot formation in ethylene nonpremixed flames, *Thirty –First* Symposium *(International) on Combustion, The Combustion Institute, Pittsburgh,* Vol. (31), (2007) 603–610.

[14] Juntao, Wu; Hoon Song Ki; Litzinger, T. Lee S.-Y.; Santoro, R.; Linevsky, M., Reduction of PAH and soot in premixed ethylene-air flames by addition of dimethyl ether, *Combustion Science and Technology*, 20, pp 837-863 178: 837–863, 2006.