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Soot Measurements in a Chlorinated Counterflow Diffusion Flame Using a Laser Scattering and Extinction Technique

Go Su Yang* and Ian M. Kennedy**

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The effects of the presence of chlorinated species on soot formation have been studied in laminar diffusion flames burning chlorinated hydrocarbons. Measurements have been made of the structure of a chlorinated laminar, diffusion flame that is stabilized in a stagnation point flow around a porous cylinder. Comparisons have been made between a pure methane flame and a flame of 50% methane and 50% methyl chloride. Temperature profiles were obtained with a thermocouple. Laser Doppler velocimetry was used to measure the velocity of the gas along the streamline. Laser extinction and scattering techniques were employed to characterize the soot aerosol. It was found that the addition of the methyl chloride to methane caused soot production, as measured by the soot volume fraction, to increase by at least an order of magnitude.

Key Words : Chlorinated Species, Soot Formation, Laminar Diffusion Flames, Laser Extinction and Scattering Techniques

1. Introduction

Chlorinated species have been studied for flame inhibition due to their characteristic scavenging reaction of H radical in the flame(Ibiricu et. al., 1964). However chlorinated species are now of more practical relevance from an air pollution and health point of view. Large parts of hazardous waste materials are reported to be solvents, which are primarily composed of chlorinated hydrocarbons and additional chlorinated species(Seeker, 1990). These chlorinated compounds are known to promote the formation of soot by increasing PAHs in flames(Karra and Senkan, 1987). The explanation that is commonly offered refers to the relatively small bond energy of Cl-C compared to the H-C bond energy. Loss of Cl from a molecule is comparatively easy and the formation of some hydrocarbon radicals in the flame is enhanced ; others may be removed by Cl scavenging e.g., H. These radical species may lead to polymerization, PAH and soot formation.

Senkan et al.(1983) investigated the impact of chlorine on soot formation in premixed methane/air flames. They found that the critical equivalence ratio at the onset of sooting decreased monotonically with chlorine content of the fuel/air mixture. However, the critical O/C ratio exhibited a much more complex behavior. McKinnon and Howard(1990) argue that this is due to a competing effect that results from variations in the stoichiometry of the premixed flames as chlorine is added.

The main objective of this work is to improve understanding of the effects of chlorine on soot formation processes by comparing between a pure methane and a mixture flames(50% of CH_3CL, 50% of CH_4). Counterflow diffusion flames have been chosen because this configuration permits rates of growth processes to be determined easily and facilitates comparisons with numerical models that may incorporate detailed chemical kinetics(Miller et al., 1984). Furthermore, the counterflow arrangement can be used to study the impact of strain rates on the production of soot and PAH in chlorinated diffusion flames. The

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* Department of Environmental Engineering, Yosu National Fisheries University, Yosu, Chonnam

** Department of Mechanical, Aeronautical And Material Engineering, University of California, Davis, California 95616, U.S.A

laser extinction and scattering theory is applied to calculate soot formation parameters such as soot particle size(D), soot number density(N) and soot volume fraction(f_v) to determine the effects of chlorine species on soot formation in hydrocarbon flames.

2. Experiments

The burner apparatus was similar to the one used by Tsuji and Yamaoka(1967). Fuel issued uniformly from the bottom of a screened burner which was housed in a duct as shown in Fig. 1. The semicircular cylindrical burner(ϕ 19 mm$\times$38 mm) formed from wrapped fine mesh screens was mounted on a mechanism with micrometer screws so that it could be moved vertically and horizontally within the air flow field. A porous plate served to create a uniform flow of air in the duct. The uniformity and turbulent intensity of the air flow were checked with a hot wire anemometer(TSI). The velocity profiles were quite flat and the intensity was measured as less than 5% of the mean across the duct. Two flames have been studied to date. The first flame served as the base case; it was a simple flame of methane burning in air. The halogen-containing species was methyl chloride(CH_3Cl) and it was mixed with methane in equal volumes to form the second flame system. Methane(99.0% pure) and methyl chloride(99.5% pure) were supplied to the porous burner from fuel cylinders and were metered by calibrated, sonic orifice flow meters.

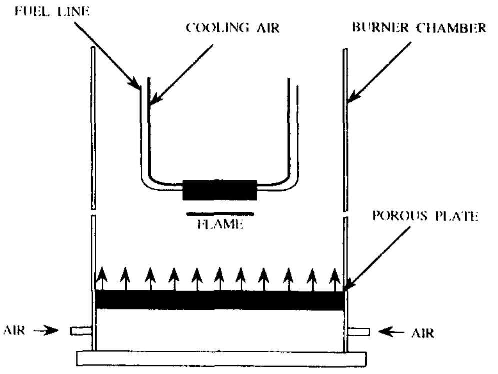


Fig. 1 Schematic diagram of cylindrical porous burner and duct

A schematic stagnation point diffusion flame is illustrated in Fig. 2. The air velocity in the duct approached the burner at velocity v, and the cylinder radius was R. The characteristic velocity gradient(nominally $a=2v/R$) was constant(38.7 s^{-1}) for both sets of measurements and the external flow at the edge of the mixing layer was given by potential flow $v_\infty = ax$. The fuel ejection velocity from the cylinder was reported in non-dimensional terms viz., $f_w = v_w(\rho_w/\rho_\infty)\ (\nu_\infty a)^{-1/2}$ where v_w was the velocity of the fuel at the cylinder wall, ρ_w was the density of the fuel at the cylinder surface and ν was the kinematic viscosity. The subscript ∞ is used to denote conditions at the edge of the flame in the approaching air stream. For pure methane flames the fuel ejection parameter f_w was -0.766; for the mixture of gases it was -2.18. The fuel ejection velocity was greater for the mixture of methane/methyl chloride(50% vo. CH_3Cl in CH_4) to ensure that the flame reaction zone was the same distance from the burner surface as with pure methane. By this means energy losses to the burner were kept the same for both flames. The adjustment in flow rates of fuel was necessitated by the change in the stoichiometric requirements of air as chlorine was added to the fuel stream.

Measurements of velocity were made along the stagnation streamline with a one dimensional LDV system. The flow was seeded with micron-

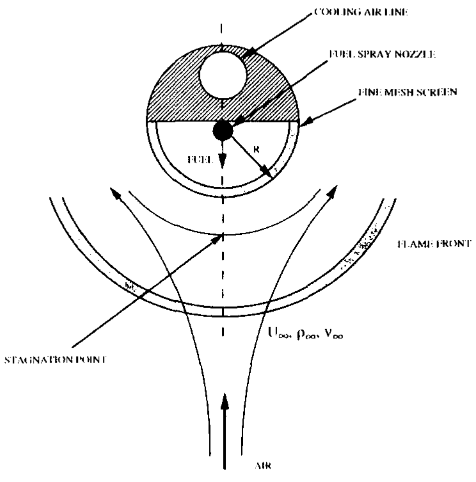


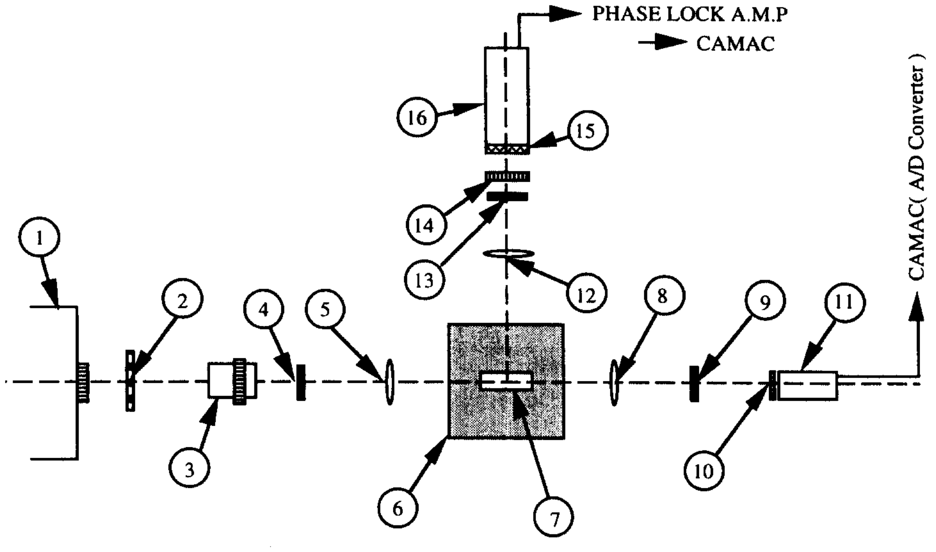
Fig. 2 Laminar counterflow diffusion flame

size magnesium oxide particles. Temperatures were measured with a fine Type S butt-welded thermocouple(wire diameter of 75 μm) which was aligned parallel to the reaction zone in order to reduce thermal conduction error ; radiation corrections were not applied in view of the uncertainty of the emissivity of the soot coated thermocouple junction. The bead was not coated(this was unnecessary in the sooty flame due to soot deposition on the bead).

A conventional laser light scattering and extinction technique(D'Alessio et. al., 1975 ; Jagoda et al., 1980 ; Kent et al., 1981) has been applied for calculating soot formation parameters, such as, soot particle size(D), number density(N), and soot volume fraction(f_v). The arrangement of the optical components is shown in Fig. 3 and was similar to that of Vandsburger et al.(1984). The light source was an Ar-ion laser operated at 488 nm with a power of $0.2\sim0.5$ W. The incoming laser beam was vertically polarized. Before entering the duct, the laser beam was modulated by a chopper wheel which provided a reference signal to a phase-lock amplifier. This procedure improved the signal-to-noise characteristics of the system. After passing through the flame the attenuation of the laser beam was measured with a photo-diode. The light scattered at 90° from a control volume in the flame was measured by a EMI 9524B Photo-Multiplier Tube(PMT). The signal from the PMT was fed to a phase-lock amplifier. A polarizer mounted in front of the PMT ensured detection of the vertically polarized component of the scattered light. Background radiation was reduced by a narrow band interference filter in front of the photo-diode and the PMT. The calibration procedure for the scattering signal was similar to those used by others(Kent et al., 1981).

3. Results and Discussion

In the Rayleigh limit($\alpha=\pi D/\lambda<0.3$; λ, laser wave length), a scattering cross-section, Q_{vv} and an extinction coefficient, K_{ext} were approximated as follows with some assumptions, such as, elastic



① : Ar-Ion LASER(488 nm)
② : CHOPPER WHEEL
③⑭ : POLARIZER
④⑨⑬ : NEUTRAL DENSITY FILTER
⑤ : CONDENSING LENS
⑥ : DUCT CHAMBER
⑦ : CYLINDRICAL BURNER
⑧⑫ : FOCUSING LENS
⑮⑩ : INTERFERENCE FILTER
⑪ : PHOTO DIODE(Extinction Signal)
⑯ : PHOTOMULTIPLIER TUBE

Fig. 3 Schematic experimental diagram for light scattering and extinction measurements scattering, monodispersed particle size, homogeneous extinction(absorption) in the flame path length.

$$Q_{vv}=\frac{\lambda^2}{4\pi^2}\left|\frac{\tilde{m}^2-1}{\tilde{m}^2+2}\right|^2\alpha^6 \tag{1}$$

$$\begin{aligned}K_{ext}&=\frac{1}{L}ln\left(\frac{I_o}{I_t}\right)\\&=-\frac{\lambda^2}{\pi}Im\left\{\frac{\tilde{m}^2-1}{\tilde{m}^2+2}\right\}N\alpha^3\end{aligned} \tag{2}$$

$\tilde{m}$ is the complex index of refraction, L is the flame path length, I_o and I_t are the initial and transmitted laser beam intensities respectively. The assumption that the soot aerosol was monodisperse in the Rayleigh limit is reasonably valid except near the stagnation point where the aerosol has grown by coagulation and surface growth and is in the Mie regime. Harris and Kennedy(1988) have shown that an assumption of a self-preserving size distribution is probably satisfactory for the soot aerosol in an atmospheric pressure flame. Adoption of this assumption would modify the reported parameters of the soot aerosol by constant factors. The complex index of refraction($\tilde{m}$) used in all calculations was $\tilde{m}=1.57\sim0.56i$. The authors knew of other published values of refractive index for chlorinated species(Janzen, 1979). However almost all published literature for the hydrocarbon diffusion flames used this number($\tilde{m}=1.57\sim0.56i$), and for the sake of comparison between CH_4 and CH_3Cl mixture with methane flames it was also adopted. The light scattering cross-sections for gas molecules(C_3H_8) obtained from the literature could be used to relate soot particle scattering signal under identical optical conditions.

$$I_{vvC_3H_8}=CQ_{vvC_3H_8}N_{vvC_3H_8} \tag{3}$$

where $I_{vvC_3H_8}$: scattering intensity from C_3H_8, $Q_{vvC_3H_8}$: scattering cross-section(total energy scattered per unit time and per unit of incident intensity) of C_3H_8, and $N_{vvC_3H_8}$: C_3H_8 gas molecule number density. From this relation, C(system constant) was determined, therefore the soot scattering signal was related to the gas value without absolute intensity determination for soot. The ratio of scattering signal from C_3H_8 to that from N_2 was measured many times to check stray beams in the system(average ratio ; 13.6). The extinction measurements were corrected for extinction of the incoming laser beam as it was transmitted through the sooty flame to the measurement point. These measurements were performed along the stagnation streamline.

The temperature profiles are shown in Fig. 4. The maximum temperature in the methane flame is 1925°K and in the mixture flame it is about 1870°K. The lower temperature in the latter case may be due to both chemical effects and radiative heat loss resulting from the presence of soot. The difference of heat of reactions between methane and the mixture(50% vol. CH_3Cl in CH_4) is 9.6 kcal/mole and may also contribute to it. However, it should be recalled that radiation corrections were not applied to the thermocouple data and these may amount to about 100°K at the peak temperatures. Furthermore, catalytic effects on the platinum thermocouple wire may give rise to some uncertainty in the reaction zone temperatures. Therefore, the difference in the measured flame temperatures is not significant given the uncertainty in the results.

Figure 5 shows the velocity distribution along the forward stagnation streamline of the burner for a pure methane flame and a mixture of 50% methane/methyl chloride by volume with the

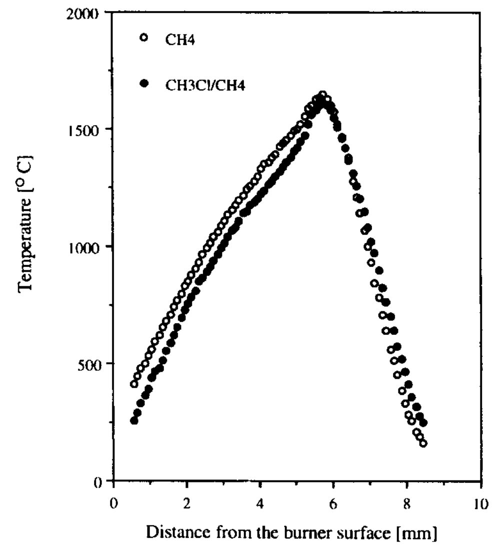


Fig. 4 Temperature profiles of CH_4 and mixture(50% CH_3Cl/CH_4) flames

same free stream gradient($a=38.7s^{-1}$). The maximum velocities of the two flames are different due to both different flame temperatures and, more importantly, the shift in the stagnation point. The stagnation point is further from the burner surface for the mixture flame as a result of its higher fuel ejection velocity from the cylinder surface. The proximity of the stagnation point to the flame front reduces the maximum velocity.

Soot profiles in the mixture flame are shown in Figs. 6~8. The methane flame did not produce measurable amounts of soot. It should be noted in these figures that the fuel flow is from the left and the air flow is from the right of the figure. The

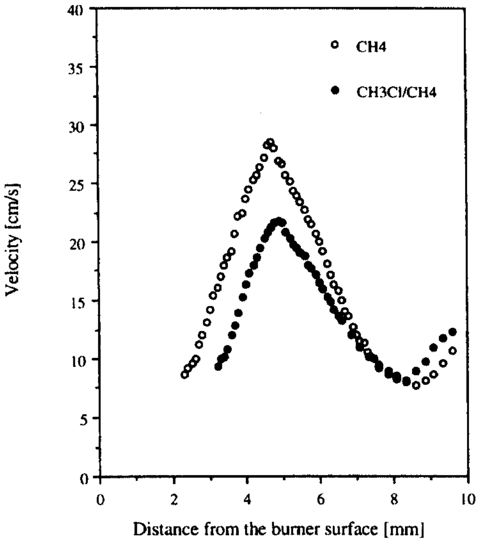


Fig. 5 Velocity profiles along the stagnation streamline for CH_4 and mixture(50% CH_3Cl/CH_4) flames

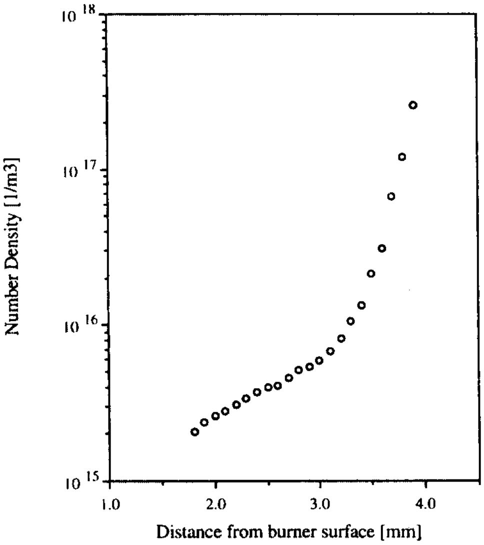


Fig. 7 Soot number density profile along the stagnation streamline for mixture(50% CH_3Cl/CH_4) flames

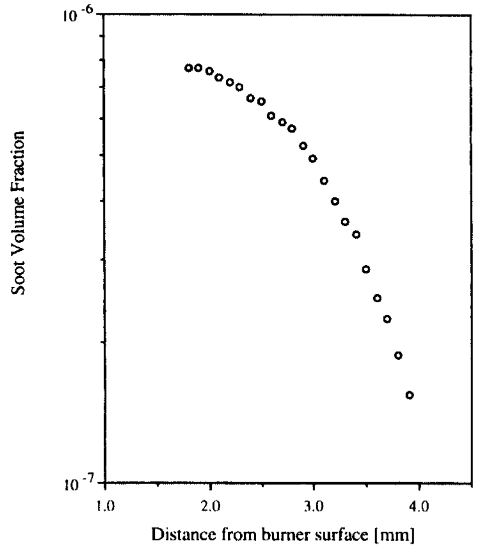


Fig. 6 Soot volume fraction profile along the stagnation streamline for mixture(50% CH_3Cl/ CH_4) flames

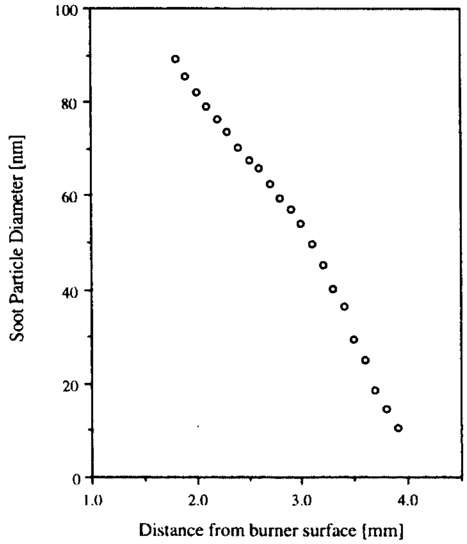


Fig. 8 Soot particle size profile along the stagnation streamline for mixture(50% CH_3Cl/CH_4) flames

usual picture of soot formation is evident in these figures, i.e., large numbers of soot particles are formed near the flame front and they are subsequently reduced in number by coagulation. Most of the soot is formed by surface growth onto existing particles as they are convected towards the stagnation point of the flow. The measured maximum soot particle diameter is 90 nm near the stagnation point. Due to this relatively large soot particle size near the stagnation region, Mie scattering is more dominant than Rayleigh scattering. The approximate equations(Rayleigh scattering) are less valid in this region as mentioned before. However the Rayleigh scattering technique is very useful and still good approximation to calculate soot parameters except near stagnation point in flames. It is worth noting in passing that particles of this size present a serious pulmonary health hazard. Figure 9 shows the profile of soot volume fraction at the stagnation points for different mixture ratios of methyl chloride to methane on a molar basis. It may be noted that the soot volume fraction increases proportionally to the concentration of chlorine compound.

Soot particles may be composed of relatively few elements such as C, H, O, N, S, etc., and the polycyclic aromatic hydrocarbons(PAHs) could be precursors of soot. PAHs, many of which have been identified to be carcinogenic and mutagenic(Longwell, 1982), have resonance structures and can survive even relatively high temperature. Therefore they could be precursors of soot particles and should increase soot formation by surface reaction. Soot formation in hydrocarbon flames may be categorized as four steps(Haynes and Wagner, 1981). The first is Particle Inception or Nucleation(particle size less than 20 Å, which is caused by condensation reactions of unsaturated hydrocarbons in gas phase, such as, C_2H_2, C_2H_{2n} and PAHs. The second step is Particle Growth Reaction(spherical shape and size about 250 Å by surface reaction and Coagulation. Surface reaction involves the attachment of gas phase species to the surface of the particles and their incorporation into the particulate phase, is one of the most important mechanisms for soot loading in a diffusion flame(Kennedy et al., 1990). The third step is agglomeration of spherical soot particles to form the characteristic chain shape structures. The final step is Oxidation of soot particles by O_2 and OH.

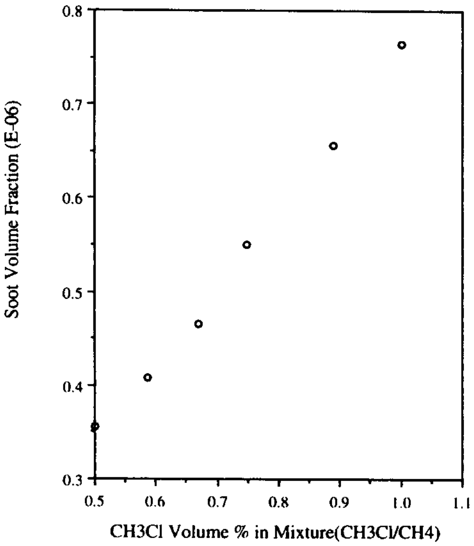


Fig. 9 Soot volume fractions at the stagnation point for different molar ratios of CH_3Cl to CH_4

These chlorinated compounds are known to promote the formation of soot by increasing PAHs in flames with comparatively easy formation of hydrocarbon radical due to the relatively lower bond energy of Cl-C than that of H-C(Karr et al., 1987). Most of the soot in any flame is formed as the result of surface growth reactions by which gas phase material is added to the soot mass. Most of this mass probably comes from acetylene and possibly from PAH addition(Lam et al., 1989). The response of the soot formation process to the addition of methyl chloride to the methane diffusion flame is remarkable. The laser scattering results show that the soot volume fraction increased by at least an order of magnitude. This figure is an estimate because the soot volume fraction in the methane flame could not be measured with the extinction method. The lower limit of detectability is about 10^{-7} and we have used this value for our comparison. The number density profile shows the typical decrease due to coagulation that has been widely observed in other sooting flames. The soot particle size is also typical of these other results but it is worth noting, from a health point of view, that these particles are in a size range which can be inhaled easily.

4. Conclusions

The results for the counterflow flame have shown that the addition of chlorine to a hydrocarbon diffusion flame has a significant impact on the formation of soot. The soot volume fraction in the flame increases by at least an order of magnitude as 50% of the methane in the fuel is replaced with methyl chloride. The soot volume fraction at the stagnation points increases proportionally to the concentration of chlorine species.

The measured maximum soot particle diameter is 90 nm near the stagnation point. Due to this large soot particle size, the Rayleigh approximation is relatively less valid in that region because Mie scattering is more dominant than Rayleigh scattering. However the Rayleigh approximation is still useful and valid to calculate soot formation parameters except near the stagnation point in flames.

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