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On the Evolution of Soot in Laminar Diffusion Flames, Part II: Effects of Carbon Dioxide Dilution in Oxygen Enhanced Environment

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Abstract

This study focuses on the effects of carbon dioxide (CO_2) dilution on the formation of soot and soot precursors in oxygen enhanced environment. Four axi-symmetric laminar coflow diffusion flames stabilized on a Yale burner are studied. CO_2 is injected either in the jet stream, or co-flow stream, or both streams. Ultraviolet and Infrared range pulsed lasers are utilised to excite soot-precursors and soot particles respectively. Time-resolved laser induced fluorescence (LIF) and laser induced incandescence (LII) are employed to emissions from excited particles. The reference flame has jet composition as 60% Ethylene/ 40% Nitrogen, and coflow composition as 21% oxygen/ 79% Nitrogen. In other flames, nitrogen is replaced with CO_2 either in jet, or in coflow, or in both streams. This replacement leads to a change in the adiabatic temperature, luminosity and flame length. It is observed that the both incandescence and fluorescence signals decreases with CO_2 dilution. It is also observed that CO_2 dilution not only shrinks the sooting region but also delays the formation of scatterers in non-sooting region. The effects of CO_2 dilution are higher when injected in the coflow stream leading to longer flames. However, when CO_2 is injected in both jet and coflow streams, the effects are further enhanced.

Introduction

This is the second part of a series of investigations aimed at providing an enhanced understanding of the mechanisms leading to soot formations in flames under conditions that involve dilution or partial premixing. In Part I, the effect of changing the oxygen content of the coflow has been investigated. It was found that both soot volume fraction (SVF) and concentration of nanostructures increase with coflow oxygen concentration up to a threshold level (27% O_2 by volume). When coflow oxygen concentration is further enhanced, SVF decreases but nanoparticles' concentration stays similar. Here, the study is extended to report the effects of dilution by carbon dioxide which is either mixed with the fuel or with the co-flow or with both.

Fuel dilution is often encountered in practical applications and definitely when exhaust gas recirculation is involved. Dilution with nitrogen is different from that with carbon dioxide due to the fact the latter breaks downs under high temperature conditions and becomes a supplier of oxygen. Several investigations have focused on the study of soot formation by introducing diluents on the oxidizer or fuel sides of flames [1-4]. A study [5] found that effects of CO_2 dilution are predominantly thermal due to temperature drop. Another study [6] reported that the chemical reactivity of CO_2 is behind the soot suppressing phenomenon. Several other studies [1, 7] have confirmed that higher CO_2 concentrations reduce soot formation. An experimental and numerical research activity [4] found that CO_2 reduces mole fraction of soot precursors which leads to a lower inception rate and soot number density. These studies have described the CO_2 effects with the help of a single parameter, soot volume fraction. This paper also considers particle concentration, growth and structural change.

Several studies [8, 9] have employed in-situ laser diagnostic techniques, such as, laser induced incandescence (LII) and laser induced fluorescence (LIF). LII is a reliable and efficient technique to track mature soot particles. It has applications from laboratory scale flames to practical combustion systems. When using LII technique, soot particles are irradiated with a high energy infrared (IR) laser beam. The soot particles absorb the laser beam, heat up and emit black body radiations which are analysed to reveal characteristics of the soot particles. The LIF technique is used to study polycyclic aromatic hydrocarbons (PAHs) and nanostructures. With appropriate laser sources and spectral filtering, difference classes of PAHs and nanoparticles can be selectively excited and analysed [10].

This study focuses on the effects of carbon dioxide dilution (jet only, coflow only, both jet and coflow streams) on soot and soot-precursors in oxygen enhanced environment. Four different 60% ethylene axi-symmetric laminar coflow diffusion flames are studied. Discussed parameters are peak soot volume fraction, concentration of soot precursors, structure and growth of soot precursors. Ultraviolet and infrared laser sources are used to excite flame particles. Time resolved LII and LIF techniques are employed to study the flame particles.

Experimental setup

Burner and flames

An axisymmetric laminar Yale burner adopted by the International Sooting Flame (ISF) Workshop is used. The burner has a fuel tube and coflow honeycomb. The fuel tube has a 4mm ID, a 0.038 mm wall thickness and is surrounded by a 75/4.76 mm OD/ID concentric co-flow honeycomb duct. Four different flames with compositions given in Table 1 are studied. The operating pressure is atmospheric in all cases, and the jet and coflow velocities are both set to 35 cm/s.

Laser sources

It is possible to selectively excite and collect emitted spectrum of a specific class of nanoparticles. This is carried out by predefining the wavelength and energy of a laser source, and by applying spectral filtering to the emitted spectrum [10]. For

example, nanoparticles (up to 20 nm) can be excited by 4th harmonic (266 nm) or 5th harmonic (213 nm). Use of 5th harmonic would include relative higher contribution from PAHs in the emitted spectrum. As this experiment is focusing on soot precursors, use of 4th harmonic is preferred [8, 9]. Similarly, it is possible to induce incandescence from soot particles either by using fundamental harmonic (1064 nm) or second harmonic (532 nm). However, use of second harmonic (532 nm) would add contributions from C_2 and C_3 bands in the emitted spectrum. As this experiment is focusing on soot particles, use of fundamental harmonic is preferred.

Flame	Chemical Composition		Flame length (mm)	Soot starting HAB (mm)	simulated adiabatic temp. (K)
	Jet stream	Coflow stream			
A	60% C_2H_4/ 40% N_2	30%O_2/ 70%N_2	31	18	2604.3
B	60% C_2H_4/ 40% CO_2	30%O_2/ 70%N_2	31	20	2551.4
C	60% C_2H_4/ 40% N_2	30%O_2/ 70%CO_2	35	25	2242.9
D	60% C_2H_4/ 40% CO_2	30%O_2/ 70%CO_2	36	28	2219.3

Table 1: Chemical composition, length, soot starting height and adiabatic flame temperature of different flames are mentioned. The adiabatic temperature is simulated using CHEMKIN.

Two laser sources were used in this study. The 4th harmonic of a mode-locked Nd:YAG Ekspla laser (266 nm, 80 ps pulse width) was used to target soot precursors. Its probe diameter and per pulse energy was 250 µm and 0.57 mJ respectively. The fundamental harmonic of a Spectra-Physics Quanta-Ray Pro-350 laser (1064 nm, 8 ns pulse width) was used to excite nanoparticles. Its probe diameter and per pulse energy was 450 µm and 1.15 mJ/. 1064 nm laser was delayed by 900 ns from 266 nm pulse to allow the same volume to be probed with both lasers.

Data acquisition and processing

Data acquisition system consisted of four photomultiplier tubes (PMTs), a spectrometer and an oscilloscope. Upon irradiance, excited particles emit radiation focused on the grating slit of a spectrometer which in turn resolves the incoming radiation spectrum into the component wavelength bands. PMTs collected the component wavelength bands in the time domain. At a later stage, the temporal response was analysed to study the formation, evolution and destruction of the excited flame particles. PMTs collected the response in narrow wavelength bandwidths such as PMT1 (266 ± 15 nm), PMT2 (350 ± 15 nm), PMT3 (445 ± 15 nm) and PMT4 (575 ± 15 nm). These wavelength bands were chosen very carefully to obtain important segments of the emitted spectrums. PMT1, PMT2, PMT3, and PMT4 recorded scattering, UV LIF, visible LIF, and LII signals respectively.

Signals from the four PMTs were recorded using a Tektronix oscilloscope (25 Giga-sample/s, 4 GHz bandwidth). At each measurement location, 500 instantaneous acquisitions were captured. An integrated signal can represent the overall response from excited particles. The magnitude of the integrated signal is related to the volume fraction of particles being probed. Signal peaks are related to mass concentration of excited species. UV LIF is originating from relatively smaller particles. Visible LIF is originating from relatively larger/rigid particles. The ratio of UV LIF to visible LIF along HAB is indicative of structural changes. Reduction in this ratio (red-shifting) may indicate particles are increasing in size or becoming rigid/graphitic. Decay of temporal response is indicative of size. Cooling rate of a particle depends on ratio of its surface area to volume which indicates larger particles will take longer to cool down. Therefore, decay value may indicate size of particles.

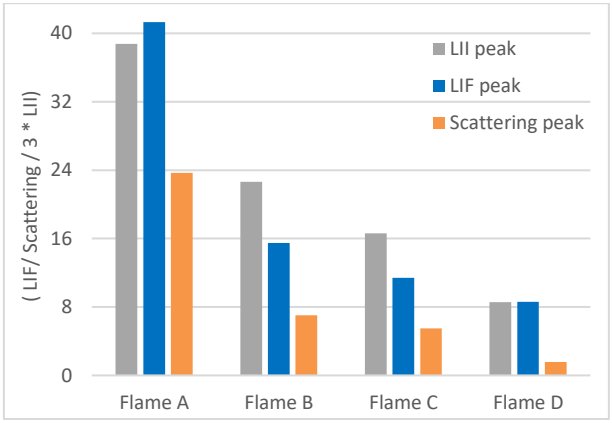

Figure 1: Peak values of laser induced incandescence (LII), laser induced fluorescence (LIF), and scattering are presented here. LII peaks in all cases are multiplied by a factor of 3.

Results

In this section, effects of carbon dioxide dilution on flame length, soot volume fraction and precursor concentration are discussed.

CO_2 dilution effects on physical characteristics of flame

Flame length is not influenced by CO_2 dilution in fuel stream. Flames A and B have similar length, 31 mm. However, flame length is increased by 16.1% when CO_2 is injected in coflow stream. Length of flames C and D is 35 and 36 mm respectively. The brightness and flame temperature also reduce by CO_2 dilution. Simulated adiabatic temperature of flames are mentioned in table 1.

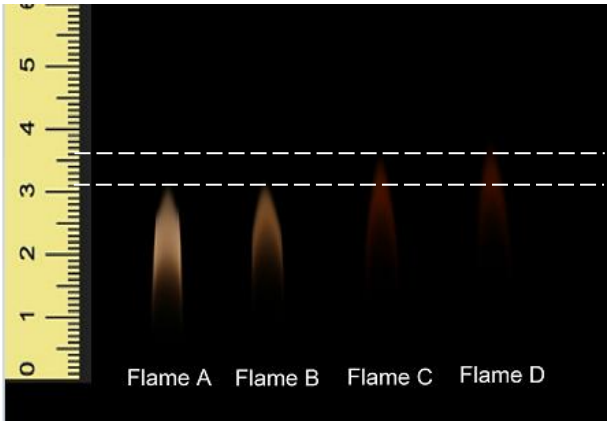

Figure 2: Flame images are presented here. Jet CO_2 dilution reduces luminosity but does not affect flame length (flame B). Coflow CO_2 dilution not only reduces the luminosity of flames (C and D) but also increases the length. Luminosity of flame C and D is very low compared to that of flame A and B. Scale in cm.

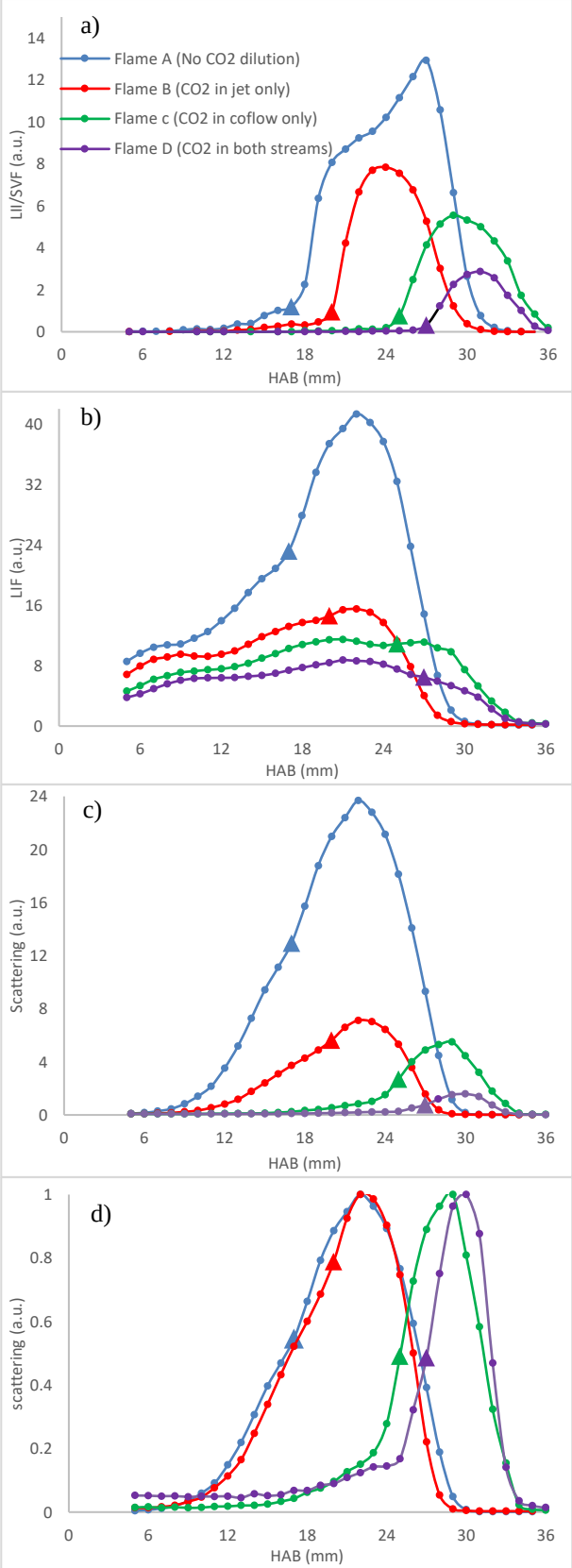

Figure 3: Laser induced incandescence, laser induced fluorescence, and scattering profiles of all flames are presented here. Triangles mark soot starting HAB. Figure 3a shows LII (SVF) signal w.r.t. HAB. Figure 3b shows concentration of nanoparticles w.r.t. HAB. Figure 3c shows scattering signal w.r.t. HAB. Figure 3d shows normalized scattering signal w.r.t. HAB.

CO_2 effects on soot volume fraction

The laser induced incandescence (LII) spectrum from 1064 nm excitation is collected in temporal domain at four distinct wavelength bins (266±15, 350±15, 445±15, 575±15 nm) using photomultiplier tubes. LII signal is proportional to soot volume fraction. Trends of LII signal collected in this study were compared with SVF trends reported by Naples group [11]. After normalization, both the trends matched well. After calibration, LII values were converted into SVF values.

Figure 3a shows integrated LII signal collected at 575 nm w.r.t. to height above burner (HAB) along the centreline of flames. The curves can be divided into two regions; a non-sooting region, and a sooting region. Boundary between the regions is marked by triangles. In sooting region, the LII signal increases with HAB until LII peak. After LII peak, oxidation region starts where LII signal gradually reduces to negligible values.

The addition of CO_2 in fuel stream (flame B), coflow stream (flame C) and both streams (flame D) reduces LII peak by 41.57%, 57.1 %, and 77.8% respectively. This indicates that soot suppressing effects of CO_2 are stronger when injected in coflow stream. When CO_2 is injected in both streams, soot suppressing effects interfere constructively.

Soot starting height increases when CO_2 is injected in fuel, coflow or both streams. Moreover, sooting area shrinks when CO_2 is injected in fuel, coflow and both streams. Soot suppressing effects due to jet and coflow CO_2 are in-line with findings of Liu [6] who studied CO_2 effects in ethylene coflow flames.

CO_2 dilution effects on concentration of precursors

266 nm laser induces a fluorescence spectrum from nanoparticles. The LIF spectrum is collected in temporal domain at four distinct wavelength bins (266±15, 350±15, 445±15, 575±15 nm) using photomultiplier tubes. Figure 3b shows peak LIF signal collected at 350nm for flames. Peak LIF signal is related to the concentration of excited nanoparticles.

Precursors concentration is significantly reduced when CO_2 is injected. Addition of CO_2 in fuel stream (flame B), coflow stream (flame C) and both streams (flame D) reduces LIF peak by 62.5%, 72.3%, and 79.3% respectively. This indicates that effects of CO_2 are stronger when injected in coflow stream. When CO_2 is injected in both streams, reduction in precursor concentration in further enhanced.

CO_2 dilution effects on scattering signal

Figure 3c shows peak LIF signal collected at 266 nm (Scattering signal). Presence of scattering signal in non-sooting regions (regions before triangles) indicates that structures other than soot may also contribute towards scattering signal. Fluorescing nanoparticles with 2-20 nm size may be present in this region [12] Scattering signal greatly reduces by addition of CO_2. Addition of CO_2 in fuel stream (flame B), coflow stream (flame C) and both streams (flame D) reduces scattering peak by 69.9%, 76.8%, and 93.3% respectively. This indicates that effects of CO_2 are stronger when injected in coflow stream. When CO_2 is injected in both streams, scattering signal is further reduced.

Discussion

Addition of a reactive gas, such as CO_2, may cause three effects; dilution effects (reduced concentration of active reactants), thermal effects (altered temperature depending on specific heat capacity), and chemical effects (different products). Varying the concentration of CO_2 can change flame temperature leading to altered chemical pathways of soot formation. At higher temperatures, CO_2 dissociates by reacting with hydrogen radicals to form hydroxyl radicals [13]

$$CO_2 + H \rightarrow OH + CO \qquad (1)$$

The chemical reaction (1) is responsible for the reduction in the concentration of soot in CO_2 diluted flame. The H radical promotes the formation and growth of soot precursors. OH radical destroys (oxidizes) soot precursors. In a CO_2 diluted flame, the H radical is consumed, and the concentration of OH radical is enhanced. Therefore, the concentration of soot precursors is reduced which results in reduced incipient soot, reduced nucleation, and reduced soot volume fraction.

Liu [6] conducted a study, using coflow oxygen concentration as 21% by volume, and found that CO_2 dilution effects are stronger when injected in coflow stream. The current study is conducted at an enhanced oxygen environment (30% oxygen by volume). As per results, soot supressing effects of CO_2 are applied in oxygen enhanced environments as well. Not only peak SVF is reduced but also sooting region is compacted by CO_2 dilution. Therefore, overall soot formation is reduced.

Figure 3b shows LIF profiles of different flames. In case of flame A (no CO_2 dilution), LIF keeps on increasing in sooting region before it drops with HAB. In case of flame B (CO_2 in jet only) LIF signal increases slightly in sooting region before it starts dropping with HAB. In case of flame C (CO_2 in coflow only), there is a plateau in LIF profile before it drops down with HAB. Plateau starts from non-sooting region and extends in sooting region. However, peak of plateau (and LIF profile) lies in non-sooting region. In case of flame D (CO_2 in both streams), LIF peak is shifted well upstream of soot starting HAB. So flames with CO_2 in coflow streams have LIF profiles peaking in non-sooting regions. Concentration of nanoparticles contributing towards LIF in sooting region is greatly reduced in case of flame D. Surprisingly, LIF of all flames is achieving peak at a similar height (HAB ≈ 22mm).

Figures 3c and 3d shows scattering and normalized scattering profiles respectively. CO_2 dilution greatly reduces scattering signal. In flame A and B (without CO_2 in coflow), scattering picks up at an early stage and grows with a slope of 7.3 before attaining peak at HAB = 21mm. In case of flames C and D (CO_2 in coflow), scattering picks up at a higher HAB and grows with a slope of 13.3 and 16.8 respectively before attaining peak at HAB ≈ 29mm. Figure 3d shows that coflow CO_2 delays the formation of scatters in non-sooting region.

Conclusion

Effects of carbon dioxide dilution on the formation of soot and soot precursors in oxygen enhanced environment have been studied. Four different 60% ethylene axi-symmetric coflow diffusion flames were investigated. Time-resolved LII and LIF techniques were employed. It has been observed that CO_2 dilution reduces SVF and concentration of nanoparticles. It was also observed that CO_2 dilution in coflow stream delays the formation of scatterers in non-sooting regions. CO_2 dilution effects are stronger when injected in coflow stream. CO_2 dilution reduces flame temperature and luminosity. When CO_2 is injected in both jet and coflow streams, the dilution effects are further enhanced. Flame length is increased by CO_2 dilution in coflow stream, regardless of jet stream dilution.

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