THE EFFECT OF CARBON DIOXIDE ADDITION ON SOOT FORMATION IN NON-PREMIXED ETHYLENE FLAMES

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Abstract
The effect of carbon dioxide addition as diluent on soot formation in ethylene/O2/Ar laminar counter flow diffusion flames has been examined. Different concentrations of CO_2 have been used in the oxidizer stream to replace argon, whereas the amount of oxygen has been kept constant. Optical techniques have been adopted to evaluate the effect of different CO2 concentrations in the oxidizer stream on the particulate production. Laser-induced fluorescence (LIF) and incandescence (LII) measurements have been used to measure concentration profiles of nanoparticle and soot in flames. Significant reductions of both soot and nanoparticles have been observed with the addition of CO_2. Increasing the amount of CO_2 used as diluent the reduction of particulate matter increases. When only CO_2 is used as diluent soot particles have been found to be completely absent, whereas nanoparticles have been detected in all the examined conditions. The net result is the reduced emission of particulate matter but enriched in harmful nanoparticles. The reduction of particle production due to the CO_2 addition can be mostly attributed to a thermal effect due to the reduced adiabatic flame temperatures at increasing amounts of CO_2 added.

Introduction

The most important concern in the combustion process is the high production of carbonaceous particles and carbon dioxide, one of the gases that contribute to the greenhouse effect. In a first analysis the particulate and CO_2 emissions could be reduced improving combustion efficiency. CO_2 emissions could be also resized by it separation and sequestration. To achieve this goal processes of pre-combustion, post-combustion and oxy-combustion are developing in order to produce as output stream only water and carbon dioxide, favoring its capture and sequestration. The oxy-combustion consists in using oxygen instead of air in combustion reactions, with extreme conditions in terms of temperatures. In this regard, water and CO_2 might be used as diluents, recycling them from the combustion products.

A number of investigations have been focused on the study of soot formation by introducing diluents on the oxidizer or fuel sides of flames [1-6]. Du et al. [1] justified the CO_2 reduction effect on soot formation with three reasons: the dilution

of reactants, a thermal effect due to the different heat capacities and a chemical influence. Shung et al [2] found that the effect of carbon dioxide is predominantly thermal, due to a decrease in the flame temperature, with no appreciable chemical influence. Du et al. [1], Liu et al. [3], Zhang et al. [4] and Gülder and Baksh [5] through experimental and numerical works, refer the chemical reactivity of CO_2 to increased production of O and OH radicals that are believed to be responsible for soot precursor oxidation.
The aim of this work is to analyze the effect of different amount of CO_2 used as diluent in the combustion process on the kinetic of hydrocarbon oxidation and pyrolysis and on the formation of particulate matter. The study has been performed in a counter-flow ethylene diffusion flame which approximates combustion occurring at the flame front of practical turbulent flames. Optical techniques are used to characterize carbon particles produced in this flame to understand the influence of the different inert on particulate production. Laser-induced fluorescence (LIF) and incandescence (LII) measurements have been used to measure concentration profiles in flames of nanoparticle and soot respectively.

Experimental procedure
The counter-flow burner used in this study was the same as that used for previous works [7-8]. The burner consists of two opposite jet nozzles (ID 2,54cm) vertically positioned. The oxidizer stream (O_2/Inerts) was introduced from the upper nozzle, while the fuel stream (C_2H_4/Ar) from the bottom. Different flames were analyzed varying the concentration of CO_2 in the oxidizer side. The fuel stream was fixed at 25% vol. C_2H_4 and 75% vol. Ar with an axial velocity of 13.2 cm/s. In the oxidizer stream the percentage of Oxygen was fixed at 22% vol. and the axial velocity at 16.1 cm/s. In a first configuration (standard case) the 78% vol. of the oxidizer side was constituted totally by Argon then the 25%, 50% and 78% was substituted with CO_2 and the remaining Argon. The distance between the two burners was maintained at 1.5 cm for all flames. With these flux velocities the stagnation plane is located around 5mm from the lower nozzle. In all the configurations the flame front was stabilized in the oxidizer plane.
Measurements were performed at different heights along the centerline. Laser Induced Emission (LIE) measurements were performed using the fourth harmonic radiation (266 nm) of a Nd:YAG laser as excitation source. Laser beam was focused in the flame and the emitted radiation was detected at 90° respect to the laser beam and was focused onto the 280 μm entrance slit of a spectrometer and detected by an intensified CCD camera (Oriel Instruments InstaSpec V ICCD). Emission spectra, averaged over 150 scans, were recorded by using acquisition time of 100 ns synchronized with the laser pulse. LIE measurements showed two broads fluorescence emissions at 330 and 440 nm, UV and visible respectively and incandescence signal, fitted by black-body radiation at 4000 K, according to literature data [9], matching the measured emission intensity values at 550 nm. Figure 1 reports emission spectra at different heights from the lower nozzle: the 4

mm spectrum corresponds to a flame region below the stagnation plane with temperature less to 1000K and high fuel concentration. 5 mm is approximately the position of the stagnation plane whereas at 6 mm high temperatures occur close to the front flame.
The UV fluorescence could be assigned to nanoparticles (2-4nm) mostly constituted by aromatic compounds constituted with 2-3 condensed rings and generally a loose structure, the second one could be due to PAH with 4-5 condensed rings and a well-organized structure. Incandescence signal is assigned at soot particles of 10-20nm and larger aggregates.

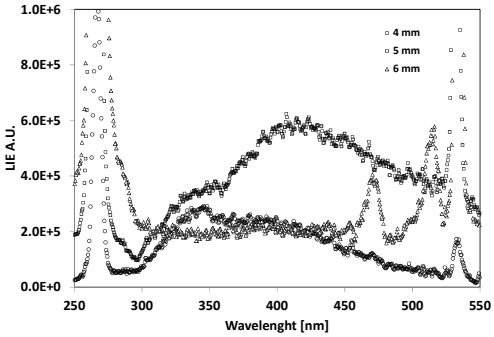

Figure 1. Laser induced emission spectra for the flame C_2H_4/Ar /O_2 collected at 4mm (circles), 5mm (squares) and 6mm (triangles) from the fuel nozzle.

Results

In a first analysis, measurements were performed using only argon as diluent for the oxidizer stream. Figure 2 shows the fluorescence and the incandescence signal profile along the flame.

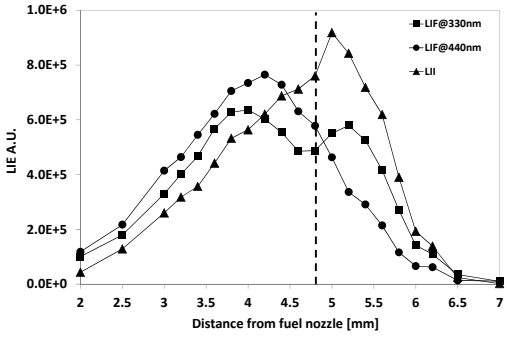

Figure 2. Laser induced emission signals as a function of the distance from the fuel nozzle for the flame C_2H_4/Ar /O_2. Stagnation plane is reported as dashed line.

Three regions can be distinguished: fuel side, stagnation plane and oxidizer region. The flame front is located in the oxidizer side in which PAH growth is due to chemical pathways. Rapid growth due the high temperature is confirmed by the fast increase of both fluorescence and incandescence signal. The stagnation plane is located around 4.8 mm from the lower nozzle; in this region the signals maximize due to both contribution from oxidizer and fuel side. In the fuel side the fluorescence and incandescence signals can be justified with pyrolysis reactions of the fuel and a physical mechanism of PAH growth (van der Waals interactions).
LIF and LII measurements were performed varying the CO_2 concentration in the oxidizer stream. In figure 3 UV fluorescence signal profiles along the flame are reported varying the CO_2 concentration in the oxidizer stream in comparison with the flame C_2H_4/Ar /O_2.

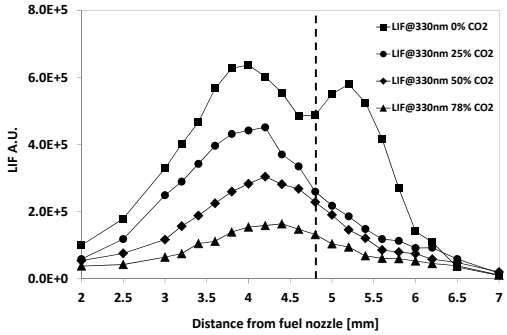

Figure 3. Laser induced fluorescence signals at 330nm as a function of the distance from the fuel nozzle for different concentration of CO_2 in the oxidizer stream. Stagnation plane is reported as dashed line.

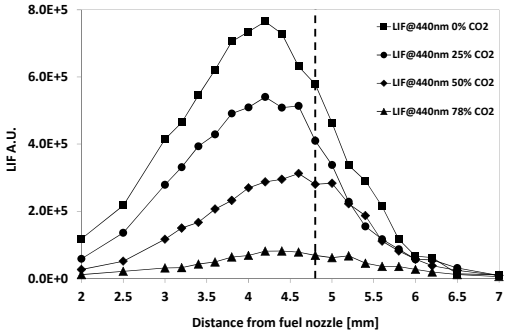

Figure 4. Laser induced fluorescence signals at 440nm as a function of the distance from the fuel nozzle for different concentration of CO_2 in the oxidizer stream. Stagnation plane is reported as dashed line.

Fluorescence can be distinguished both in fuel and oxidizer side. Overall it can be noticed a strong reduction of the signals with respect to the flame C_2H_4/Ar /O_2.

Fluorescence signal in the oxidizer side is reduced from the CO_2 addition. Only when 78% CO_2 is added the signal is strongly reduced also in the pyrolytic zone. Figure 4 show the trends of visible fluorescence signals with the addition of CO_2. The fluorescence at 440 nm maximizes the signal in the pyrolytic zone of the flame, being related to nanostructure formed by large PAHs at low temperatures. The reduction of both UV and visible fluorescence increases as CO_2 content increases, being still detectable when only CO_2 is used as diluent.

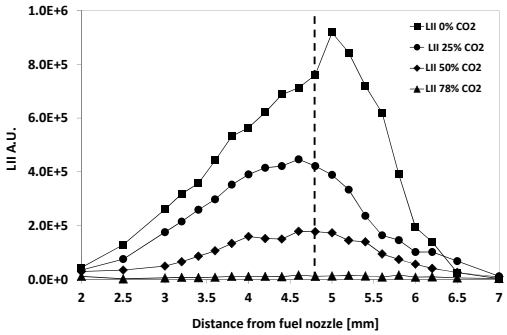

Figure 5. Laser induced incandescence signals as a function of the distance from the fuel nozzle for different concentration of CO_2 in the oxidizer stream. Stagnation plane is reported as dashed line.

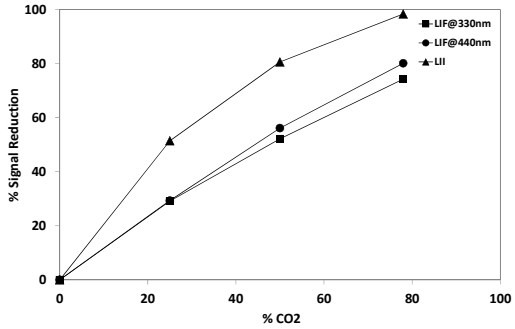

Figure 6. Percentage reduction of laser induced emission signal as a function of the CO_2 concentration in the oxidizer stream.

Figure 5 shows the trends of laser induced incandescence signals with the addition of CO_2. Incandescence signals show the same behavior found for fluorescence signals but when the 78% CO_2 was added the incandescence signal is below the uncertainty of the experimental measurements and it means the soot absence.
The CO_2 adding effect can be justified with considerations on the adiabatic flame temperature: adding CO_2 a reduction in the adiabatic flame temperature is registered because of its lower specific heat with respect to Argon.

Figure 6 shows the percentage reduction of fluorescence and incandescence signals as a function of CO_2 concentration in the oxidizer stream. A totally incandescence reduction is registered after 78% CO_2 is added to the oxidizer stream while 70-80% fluorescence reduction is observed.

Conclusions

Optical diagnostics were used to understand the effect of different amount of CO2 as diluent in a counter flow ethylene diffusion flame. Both LIF and LII were performed in order to detect both nanoparticles and large soot aggregates respectively. CO_2 was added in the oxidizer stream up to 78% vol. of the total flux. No qualitative variations of fluorescence and incandescence trends were found along the centerline of the burner. The CO_2 addition strongly reduces fluorescence and incandescence signals in the fuel side and in the oxidizer side. However, while incandescence, i.e. soot aggregates are completely depleted when only CO_2 was used as diluent, fluorescence signal, i.e. nanoparticles, were still detected in the flame. Considerations on the adiabatic flame temperatures can help to justify the effect of CO2 addition: the lower specific heat of CO_2 respect to argon one causes a reduction larger than 200°C in the adiabatic flame temperature.

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References

[1] Du DX, Axelbaum RL, Law CK. The influence of carbon dioxide and oxygen as additives on soot formation in diffusion flames. Proc Combust Inst 1990; 23:1501–7.

[2] Schug KP, Manheimer-Timnat Y, Yaccarino P, Glassman I. Sooting behaviour of gaseous hydrocarbon diffusion flames and the influence of additives. Combust Sci Technol 1980; 22:235–50.

[3] Liu F, Guo H, Smallwood GJ, Gülder ÖL. The chemical effects of carbon dioxide as an additive in an ethylene diffusion flame: implications for soot and NOx formation. Combust Flame 2001; 125:778–87.

[4] Zhang C, Atreya A, Lee K, Symp. Int. Combust. 24 (1) (1992) 1049–1057.

[5] Gülder ÖL, Baksh MF, Influence of carbon dioxide dilution on soot formation in diffusive combustion. Combustion Institute Canadian Section, Quebec, QC, 1993, pp. 40-1–40-5.

[6] Ni T, Gupta SB, Santoro RJ. Suppression of soot formation in ethane laminar diffusion flames by chemical additives. Proc Combust Instit 1994; 25:585.

[7] D'Anna A, Commodo M, Sirignano M, Minutolo P, Pagliara R. Particle formation in opposed-flow diffusion flames of ethylene: An experimental and numerical study. Proceedings of the Combustion Institute 32 (2009) 793–801

[8] Sirignano M, Collina A, Commodo M, Minutolo P, D'Anna A. Detection of aromatic hydrocarbons and incipient particles in an opposed-flow flame of ethylene by spectral and time-resolved laser induced emission spectroscopy. Combustion and Flame 159 (2012) 1663–1669

[9] Commodo M, Violi S, D'Anna A, D'Alessio A, Allouis C, Beretta F, Minutolo P. Combust. Sci. Technol. 179 (2007) 387–400.

10.4405/35proci2012.VI10