Chemical and thermal effects of CO_2 addition in fuel-rich premixed ethylene flames

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The presence of non-fuel compounds in the fuel stream of an industrial burner can strongly modify the pollutant formation. In fact, a massive recycle of burnt gases, mainly constituted by CO_2 and H_2O, is currently used in several new technologies with the attempt to reduce NO_x and soot emissions, such as FGR (Flue Gas Recirculation) or FC (Flameless Combustion). For this reason, in this work an experimental and computational study on the effect of a CO_2 addition to premixed laminar flames has been carried out, in order to highlight its chemical and thermal effects on the kinetic pathways that lead up to the formation of airborne polluting agents, in particular *soot*, Polycyclic Aromatic Hydrocarbons (*PAH*), and their precursors. In order to obtain quantitative information concerning fuel-rich combustion processes, experiments have been carried out, on a laboratory scale apparatus, by using a water-cooled porous McKenna burner, working at atmospheric pressure, coupled with a probe-based in-flame sampling system and with chromatographic and gravimetric analytical techniques, this was done in order to collect and analyze the combustion products found in gas phase (O_2, CO, CO_2, C_1-C_6 hydrocarbons), liquid phase (PAH) and solid phase (soot), respectively. The effect of CO_2 addition has been examined taking as a reference an undoped ethylene/O_2/N_2 fuel-rich premixed flame (having equivalence ratio ϕ equal to 2.76 and cold gas flow velocity equal to 4.9 cm/s) while replacing the 30% of N_2 by an equivalent amount of CO_2, obtaining an ethylene/O_2/N_2/CO_2 flame. Several experimental findings have been directly compared to model predictions, performed with the PREMIX code of the DSMOKE software package, using detailed kinetic mechanisms able both to describe hydrocarbons oxidation and pyrolysis and to isolate the different effects of CO_2 addition. A comparison between modeling results suggests that the presence of carbon dioxide in the combustion environment can have direct implications in the chemical reduction of soot and PAH production tendencies because it causes, throught the promotion of the main reaction $CO_2+H \rightarrow CO+OH$, an enhanced presence of OH radicals in the post-flame zone, which can be responsible for the oxidation of PAH, soot and mainly for the chemical destruction of their gaseous precursors.

1. Introduction

Particulate matter emissions, produced by combustion applications, are of particular concern for the environment (pollution), the public health (toxicology) and the efficiency of thermal processes (energy saving). Therefore, an important research field consists of identification and understanding of the chemical effects of soot suppressors. Main practical effects of various additives, that can be reactive, slightly reactive or simply inert, have been investigated in diffusion flames, stabilized either on coflowing or on counterflowing burners, because they correspond more closely to practical burning systems.

The effect of carbon dioxide as an in-flame additive have been investigated in the past on hydrocarbon diffusion flames: these experiments showed that the addition of CO_2 to the fuel or the oxidizer side has chemical, dilution and thermal effects on soot formation. The chemical effect of CO_2 addition on soot and NO_x formation has been focused by Liu et al. (2001) in a counterflow ethylene diffusion flame by using detailed chemistry and trasport properties models. Simulation findings suggest that the chemical effects of CO_2 addition on the reduction of sooting tendency can be ascribed to a reduced acetylene concentration and an enhanced oxidative attack of particulate precursor due to O and OH radicals in soot formation region. Several studies have been performed on premixed flat flames of different hydrocarbons, operated at atmospheric pressure, but only few of them (Haynes et al. (1982), Vandooren et al. (1998)) have been devoted to the understanding of the chemical effect of soot and PAH inhibitors, such as carbon dioxide. Motivated by these issues, a laboratory-scale experimental study has been carried out on laminar premixed ethylene/air and ethylene/O_2/N_2/CO_2 fuel-rich flames, in order to obtain information on the influence a gaseous additive on the reactions pathways involved in the formation of soot and its precursors. Finally, detailed kinetic schemes describing hydrocarbon oxidation and pyrolysis have been used to simulate the investigated flames. Model computations were also able to isolate the thermal and chemical effects of CO_2 addition, thus providing some interesting suggestions about the effective influence of this additive in PAH and soot formation, confirming and clarifying the experimental evidences.

2. Experimental: main results

In order to obtain quantitative information concerning main pollutants emissions caused by a fuel-rich combustion process, two laminar premixed flat flames, ethylene/air and ethylene/N_2/CO_2/O_2, have been experimentally studied on a water-cooled McKenna burner. The burner is constituted by a stainless steel porous plate (60 mm diameter), where the reactants mixture is fed, surrounded by a coaxial bronze porous ring flushed with nitrogen to shield the flame from atmospheric oxygen (Mancarella et al., 2006).

As a premixed fuel and oxidizer mixture is used, a turbulence generating grids tube has been set upstream the burner to obtain a homogeneous feed composition along the burner radial co-ordinate. A stainless steel disk (60 mm diameter) has been located 20 mm above the burner surface, in order to stabilize the flame in its upper part. The effect of CO_2 addition has been examined taking as a reference an undoped ethylene/air fuel-rich premixed flame (Mancarella et al., 2006) and replacing about 30% by vol. of N_2 (oxidizer-side) with an equivalent amount of CO_2, resulting in an ethylene/O_2/N_2/CO_2 flame. Keeping constant the cold-gas flow velocity (4.9 cm/s) and the C/O ratio (0.92) for the investigated flames, it was possible to directly compare the concentration profiles for main species involved in the combustion process and to point out alterations in pollutant emissions due to an additive in-flame chemical and thermal effect. Some fundamental parameters of the inlet mixture for the investigated flames are listed in Table 1.

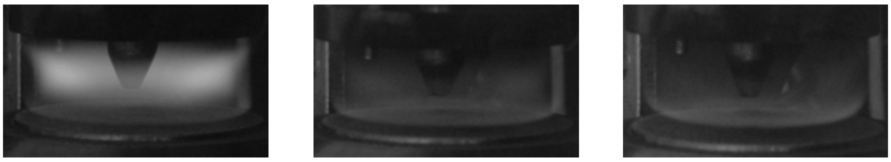
An isokinetic products sampling has been carried out by introducing an oil-cooled stainless steel probe inside the flame at different heights above the burner (HABs).

Condensable Species (CS) are separated from gaseous compounds in an ice-cooled trap, while soot is collected on a PTFE filter (pore size: 200 nm) placed between two stainless steel AISI316 flanges; finally, sampled gases have been analyzed by on-line gas chromatography (Perkin Elmer Clarus500), using thermal conductivity (TCD) and flame ionization (FID) detectors, for the detection of permanent gases (O_2, CO, CO_2) and light hydrocarbons (C_1-C_6), respectively. CS collected inside the cold trap are extracted with acetonitrile to separate soluble compounds from the insoluble carbonaceous material defined as soot. Therefore, the overall soot amount is detected gravimetrically, while PAH (up to about 300 amu) in the condensed phase are measured by liquid chromatography on a Jasco PU-1580 HPLC.
At least, temperature measurements within the investigated flames were performed using a Pt/Pt-Rh (13%) micro-thermocouple (wires diameter = 25 μm, length = 15 cm) located in a thin alumina sheath. Temperatures data are not corrected for radiation losses.

Table. 1. Main compositional values for the flames characterized in this study.

	C_2H_4 % vol.	O_2 % vol.	N_2 % vol.	CO_2 % vol.
Flame 1	16.2	17.6	66.2	-
Flame 2	16.2	17.6	46.3	19.9

In this study, the influence of carbon dioxide in an ethylene fuel-rich flame has been experimentally focused on laminar premixed flame structure and PAH and soot formation investigations. Considering the macroscopic features of the substituted flames (flame 2 and 3), reported in figure 1, it is possible to notice that the partial replacement of N_2 with CO_2 causes a marked post-flame luminosity intensity drop, index of in-flame soot content reduction, coupled with a red-like color tendency, due to the increased presence of optically active molecules whithin combustion products. Moreover the flame stability is strongly affected by the CO_2 presence in the cold inlet mixture: in fact, for substitution of N_2 with an equivalent amount of CO_2 higher than 50% an increasing both flame front shift to higher HABs and flame instability take place. It is well-known that, due to its physical and chemical properties, carbon dioxide causes flame propagation inhibition.



Flame 1 ***Flame 2*** ***Flame 3***

Reference flame ***30%N_2→CO_2*** ***50%N_2→CO_2***

Figure 1. Aspect of the investigated flames.

Several changes in PAH and soot in-flame concentrations have been noticed in the CO_2-doped flame. PAH and soot suppression indexes can be useful to highlight how the presence of CO_2 can globally reduce pollutants emissions. Such an index has been calculated taking as a reference the ∑PAH concentration and soot concentration data obtained for the undoped ethylene/air flame and their trends have been reported in figure 2(A) and 2(B), respectively. Analyzing these figures it can be clearly seen that the presence of carbon dioxide causes an overall in-flame PAH and soot content reduction, of about 75% and 30% respectively. The absolute PAH and soot concentration variations did not imply modifications in their trends: the shape of PAH and soot concentration profiles, in fact, are quite similar for doped and undoped flames. This fact suggests that the presence of CO_2 is not able to affect PAH and soot growth dynamics but only causes their post-flame consumption and the reduction of their precursors.

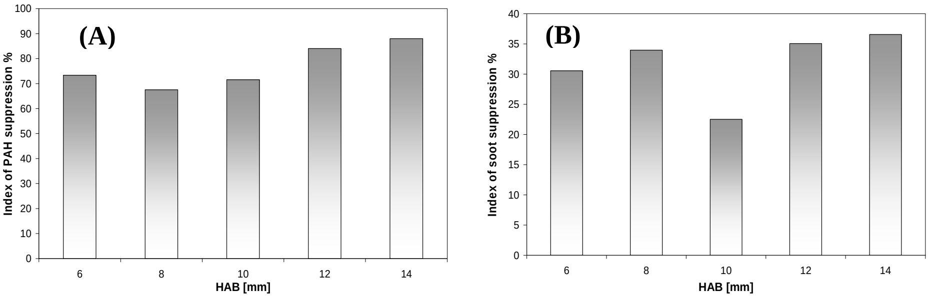


Figure 2: Trends of ∑IPA *(A) and soot (B) suppression indexes for flames with and without an oxidizer-side carbon dioxide dilution.*

3. Kinetic modeling: results and discussion

As discussed by Du et al. (1995), the introduction of an additive to a flame generally affects soot formation through the following three paths: (1) dilution effect because of reduction in the concentration of the reactive species; (2) thermal effect because of the change in flame temperatures; and (3) the direct chemical effect because of the participation of the additive in chemical reactions related to soot formation and oxidation. In our study, the substitution of the 30% v/v of N_2 with an equivalent amount of CO_2 allows for neglecting the dilution effect but not the thermal and chemical effects, which occur simultaneously and are intimately coupled. Experimentally it is impossible to completely decouple the change in flame temperatures caused by the physical properties of the additive, from that caused by its chemical features. Although it has been experimentally established that the addition of CO_2 reduces PAH and soot emissions in laminar premixed ethylene flat flames, as discussed in the previous session, the mechanism that causes this phenomenon remains unclear. As suggested by Liu et al. (2001), a similar numerical strategy was developed to identify the chemical effects of carbon dioxide introduced as a diluting agent, in this case to laminar premixed flames and not to counterflow diffusion flames. Two numerical simulations need to be obtained: one is for the presence of the reactant CO_2 (in the sense that the specie is allowed to participate in chemical reactions). The other is for the presence of the fictitious CO_2, referred in the following as FCO_2. The fictitious CO_2 is defined as a chemical species having exactly the same thermochemical and transport properties of the reactant CO_2 but it is not allowed to participate in the chemical reactions, that is, chemically inert. Differences between the two solutions are therefore entirely attributed to the chemical effects of carbon dioxide.

The detailed kinetic mechanism used for this study is the POLIMI (Ranzi et al. (2001)) model, which is able to describe hydrocarbons oxydation and pyrolisis. All the model computations were carried out with the premixed code of the Dsmoke software package using the experimental temperature profiles corrected on the basis of the correction found for the C_2H_4/air flame, which was used as a reference. In particular the temperature profile of this flame has been preliminarily corrected to allow for a good match between experimental and computed benzene profiles. Modifications made on the C_2H_4/air flame temperature profile have been then applied for the CO_2-containing flame. This type of thermal field modification is necessary because it allows to take into account the probe effects, which causes flame perturbations and in particular is able to lower the local flame temperature, as discussed by Hartlieb et al. (2000). The exactly-same corrected temperature profile has been used for the numerical simulations regarding the reactant and the fictitious CO_2. A comparison between the calculated adiabatic flame temperature, the experimental temperature profiles and the corrected ones, for the investigated flames, is reported in figure 3(A).

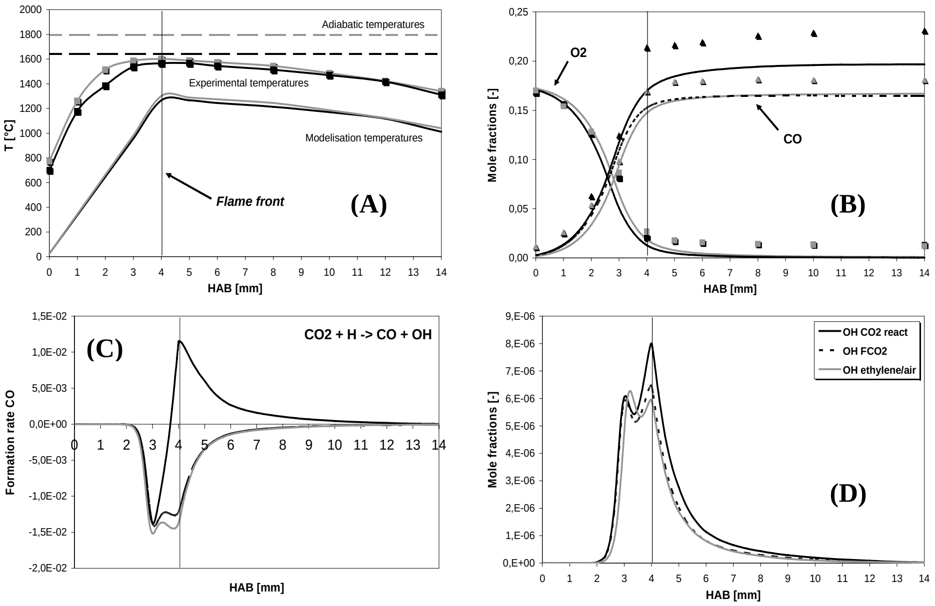


Figure 3: (A) Comparison between adiabatic flame temperatures (dotted lines), experimental temperatures (continous lines with markers) and modelisation temperatures (continous lines) for the ethylene/O_2/N_2 (gray) and ethylene/O_2/N_2/CO_2 (black) flames. (B) Experimental and modeling O_2 and CO concentration data: simbols indicate experimental values, continous line indicate the predictions obtained with the CO_2-reactant model and the dotted line indicate the fictitious CO_2 one. (C) Modeling prediction of the net rate of CO formation for the key-reaction $CO_2+H \rightarrow CO+OH$. (D) Modeling predictions for the OH radical concentration profiles.

If we preliminarily consider figure 3(A) it is possible to anticipate that the effect of the CO_2 substitution on PAH and soot is mainly chemical: the differences between the temperature values for flame 1 and flame 2 are not so relevant, especially in the post-flame zone (the flame front can be located at HAB=4 mm), where we experimentally detect most of the changes in the pollutants concentration profiles.

The presence of CO_2 practically leaves unchanged the reactants consumption dynamic (for example, oxygen concentration profiles are presented in figure 3(B)) but strongly affects the carbon monoxide formation. Considering figure 3(B) and 3(C) it can be clearly seen that this phenomenon is purely chemical and it can be ascribed to the promotion of the key-reaction $CO_2+H \rightarrow CO+OH$. As a consequence, the presence of CO_2 is able to chemically enhance the OH radical in-flame formation: in figure 3(D) it can be seen that the predicted OH maximum concentration value for the CO_2-reactant model is higher that the CO_2-fictitiuos one. The higher OH post-flame concentration can be responsible for the PAH and soot burnout and for the direct oxydative attack of their gaseous hydrocarbon precursors, especially C_2H_2 and benzene, as the experimental results clearly revealed.

4. Conclusions

The presence of in-flame gaseous additives can strongly modify the pollutants formation, according to different mechanisms (dilution, flame temperature modifications and effective partecipation in the chemical reaction pathways). In this work several experimental investigations have been carried out concerning the use of carbon dioxide as an additive in laminar premixed flat flames. A $C_2H_4/O_2/N_2/CO_2$ flame, obtained with an oxidizer-side sobstitution of about 30% of N_2 of an ethylene/N_2/O_2 reference flame with an equivalent amount of CO_2, have been studied. In order to clarify experimental evidences regarding the effect of this gaseous additive on PAH and soot formation, a computational work have been also carried out, using a modeling procedure that allows to identify the relative contribution of the thermal and the chemical effects caused by such an additive in-flame presence. The direct comparison between experimental and modeling findings suggests that CO_2 is able to chemically reduce PAH and soot emissions, improving OH oxydative attack of PAH, soot particles and their gaseous precursors.

5. References

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