THE EFFECT OF OZONE ON SOOT FORMATION IN PARTIALLY PREMIXED LAMINAR METHANE/AIR FLAMES

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Abstract

Soot is globally considered as a strongly harmful compound to people's health as to the environment [1]. For this reason, the identification of technologies and methods able to reduce the release of soot particles is a hot topic in the research field. The introduction of active molecules in the burners seems to have a strong potential and among them, ozone represents a good candidate. In this study, the effect of ozone addition on soot formation in partially premixed laminar methane flame has been investigated. Two equivalence ratios (Φ) were analyzed, equal to 15 and 25, respectively. Soot particles collected in the centerline of the flames at several heights above the burner have been examined in terms of size, morphology, and chemical/structural characteristics, by differential mobility analysis, atomic force microscopy, and Raman spectroscopy respectively. The Raman spectroscopy analysis indicates that ozone addition promotes the formation of slightly larger aromatic soot constituents. Moreover, within the selected experimental conditions and ozone concentration of several hundred parts per million, the flame temperature is unaffected regardless of the presence or absence of ozone. Consequently, it can be inferred that the observed modifications in soot characteristics are predominantly attributed to chemical factors. The observed effects are all consistent with a possible chemical interaction of atomic oxygen, resulting from the decomposition of ozone in the post-flame zone, with aromatic π-radicals, precursors of the soot particles.

Introduction

Combustion of hydrocarbon fuels plays a central role in our everyday life, but the understanding of the mechanisms involved in this process is an active and ongoing research field. In the last decades, great attention has been given to the investigation of the byproducts of incomplete combustion, especially soot. Soot particles can strongly differ in terms of size, nanostructure, and chemical composition according

to the combustion conditions. Factors influencing this variability include flame temperature, fuel composition, pressure, residence time, and premixing level. Innovative experimental [2-4] and theoretical methods [5,6] have recently contributed to enrich our comprehension of soot formation and evolution in flame. A significant breakthrough stands in the identification of π-radicals as critical intermediates in the inception and growth of soot particles. Recent investigations supported the existence of molecular clustering reaction pathways driven by radical-chain reactions of π-radicals whose understanding could strongly contribute to the clarification of the main mechanisms involving soot formation [2,5].
Several studies investigated the soot formation in purely diffusive flames [7-10], but the analysis of partially premixed flames can be extremely useful due to the use of this type of flame in a large class of practical devices.

Experimental Setup

A partially premixed flame arises when the fuel is mixed with a sub-stoichiometric amount of air - to generate a local fuel-rich mixture - before reaching the reaction zone, where additional air becomes available. The effects of partial premixing on soot formation have been explored using diverse techniques [11-14]. In this work, the effect of ozone on particle nucleation and soot formation is analyzed by investigating a partially premixed laminar flame of methane and air, operated at two different equivalence ratios, i.e. different amounts of the primary air added to the fuel stream, equal to 15 and 25, respectively. The experimental conditions are reported in Table 1.

Table 1. Experimental Conditions.

Flame	**Φ**	**O_3 [ppm]**	**Q_{CH4} [l/min]**	**Q_{PA} [l/min]**	**Q_{SA} [Nl/nh]**
$\Phi15$	15	-	0.4	0.50	4000
$\Phi15_{O3}$	15	570	0.4	0.50	4000
$\Phi25$	25	-	0.4	0.32	4000
$\Phi25_{O3}$	25	500	0.4	0.32	4000

The fuel flow rate (Q_{CH4}) remains constant for both flames, as does the secondary air flow rate (Q_{SA}), which is provided to stabilize the flame. The variable factor is the primary air flow (Q_{PA}), responsible for generating the two Φ values. The burner was the same as in previous studies [14]; a schematic representation is reported in Figure 1. The ozone was produced by an ozone generator Model 1001 Jelight Company Inc. For both flames, the ozone concentrations were dictated by the limitations of the ozone generator, which grantees a maximum conversion of oxygen into ozone equal to 0.25% c.a. The resulting concentrations were measured via a Model 205 Dual Beam Ozone Monitor (2B Technologies).

The exhausts of the flames were collected using a horizontal stainless steel tubular probe with a 1 cm outer diameter and an orifice of 0.2 mm. A turbulent N_2 diluent flow was provided so to avoid particle aggregation and quench chemical reactions of the flame exhausts. The flame products were collected at different heights above the burner (Z), so to have a clear picture of the evolution of the particles in the flame.

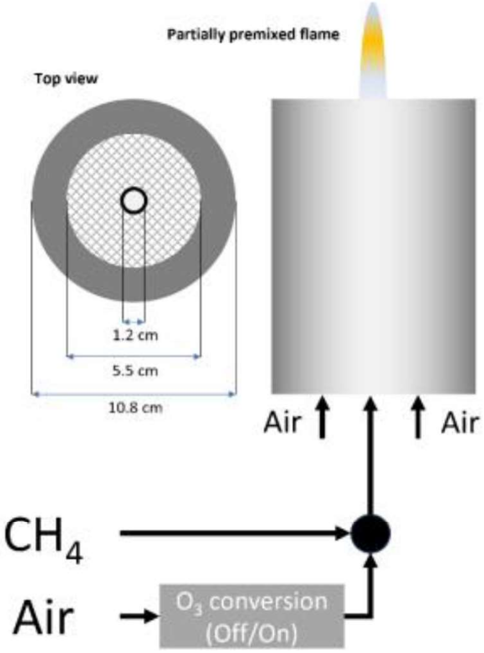

Figure 1. Schematic of the co-flow partially premixed burner setup.

Results

For each flame, the analysis of the effects of ozone on the produced soot was performed by using RTD signal analysis, particle size distribution function investigations, temperature measurements, semi-contact AFM, and Raman Spectroscopy.

Temperature does not significantly change after the introduction of ozone, probably due to the low concentrations involved in this study.

As reported in Figure 2, for both equivalence ratios, PSDs register a decrease in particle number in the upper part of the flame. This can be due either to a higher oxidation reactivity of the soot from ozone addition compared to the normal one, or a lower concentration and nucleation of soot because of the ozone injection into the flames.

Semi-contact AFM allows to investigate the morphology of the soot particles, highlighting a larger number of collected particles, surface coverage, and collected volume of the particles for higher equivalence ratios. 3-dimensional visualization of the AFM images shows a lower height of the collected particles in the ozone-doped flame. It is notable that the heights of the particles collected in the flames after ozone addition correspond to that of PAHs of only a few layers (bin spacing approximately corresponding to the PAHs interlayer distance). Moreover, the base radius follows the same trend, decreasing with reducing Φ and with ozone.

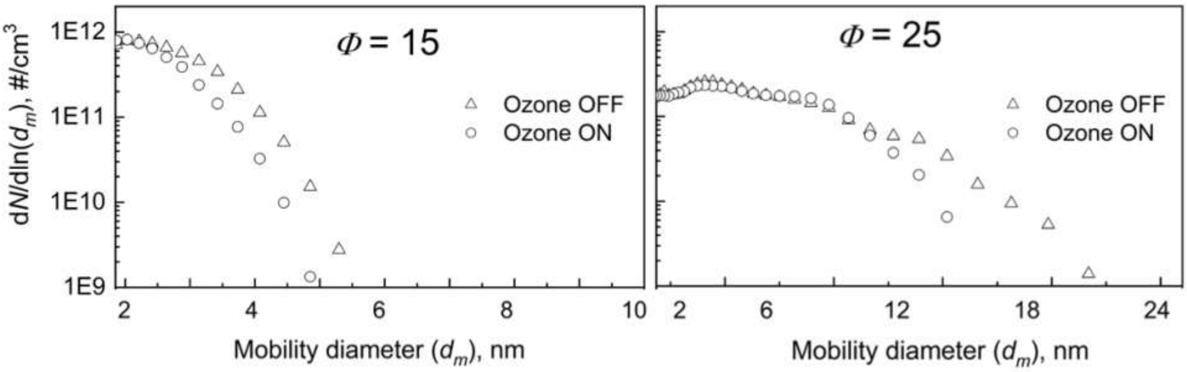

Figure 2. Particle size distributions (PSDs) along the flame centerline with and without ozone injection collected at Z= 49 mm. Φ equal to 15 and 25 are reported on the left and right side, respectively.

Raman spectroscopy has been used to assess the effect of ozone addition on soot chemical/structural characteristics. O_3 promotes the growth of the aromatic size, evidenced by the larger D/G ratio and a better graphitic structure shown by the deeper valley between D and G peaks. This effect can be tentatively assigned to the removal of resonantly stabilized radicals. In fact, in the flame without O_3, a higher amount of such radicals, which arise from non-hexagonal defects, would favour crosslinks between aromatics and, thereby, reduce HACA growth producing smaller aromatic structures. The observed effect when introducing ozone is consistent with a chemical interaction of atomic oxygen with aromatic π-radicals, precursors of the soot particles, resulting in a reduced clusterization of soot molecular constituents. Furthermore, the interaction of the atomic oxygen with the aromatic π-radicals in incipient particles can also alter their growth through coagulation.

Conclusions

This study aims to investigate the effects of ozone in flame. From these results, the introduction of O_3 in flame and the consequent presence of atomic oxygen seems to affect the soot formation mechanisms. For each flame condition, soot particles show an altered number and dimension after the introduction of the active molecule, as well as different morphology and chemical structure. Further analysis is currently investigation so to highlight the main variables affecting the production of soot and to univocally individuate an innovative combustion methodology able to reduce pollutant emissions [15,16].

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