The effect of ozone addition on laminar flame speed

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ABSTRACT

The effect of ozone (O_3) addition on laminar flame speeds (S_L) across a wide pressure range was investigated experimentally and numerically using three fuels, CH_4, C_2H_4 and C_3H_8. Enhancement of S_L due to O_3 addition was consistently observed for CH_4 and C_3H_8 mixtures over a range of lean to rich equivalence ratios, based on comparisons of S_L measured with and without O_3 addition. For both fuels, simulation results agree with experimental results, with the best predictions at near stoichiometric conditions and the largest discrepancies for fuel-rich cases. A significant increase in the S_L enhancement was observed at elevated pressures: the enhancement in the measured S_L for a stoichiometric CH_4/air mixture with 6334 parts per million (ppm) O_3 addition increased from 7.7% at atmospheric pressure to 11% at 2.5 atm. Elevated pressure both promotes O_3 decomposition, which provides O atoms, and suppresses diffusion of H, which reduces the influence of the O_3+H=OH+O_2 reaction. Together, these lead to the increased S_L enhancement with pressure. In contrast to the results for the two saturated hydrocarbons, both detrimental and beneficial effects due to O_3 addition were observed for the unsaturated hydrocarbon fuel, C_2H_4 in this study. With O_3 addition, C_2H_4/air S_L decreased at room temperature and pressure, owing to the heat loss induced by the exothermic ozonolysis reaction between O_3 and C_2H_4 in the mixing process, but increased as the ozonolysis reactions were minimized when reactants were cooled to 200 K or pressure was decreased below 0.66 atm. These experimental results were successfully explained by a numerical model that includes a new ozonolysis sub-mechanism.

1. Introduction

Non-equilibrium plasma assisted combustion (PAC) has shown potential for enhancing and controlling combustion processes [1,2]. It has been reported that PAC can reduce ignition delay times [3], increase strain rates at which extinction occurs [4], increase flame propagation speeds [5], improve flame stabilization [6], and suppress soot formation [7,8]. Unfortunately, the operating conditions of non-equilibrium plasma and combustion systems are not well aligned. Most combustion systems operate at elevated pressure conditions, while non-equilibrium plasmas favor pressures below 1 atm [9]. High pressure causes plasma thermal instability, non-uniform structure [1], and collisional thermalization of the discharge [9]. At the same time, radicals have a shorter lifetime at higher pressure [10], and thus they are generally quenched before being transported to the reaction zone (if generation is not *in situ*). The difficulty of generating stable, uniform, non-equilibrium plasmas at high pressures can be mitigated by the injection of long-lived, plasma-produced species. One attractive species is ozone (O_3), which can be produced efficiently at high

pressure and has a sufficient lifetime to be transported to the flame region to enhance fuel oxidation.

Previous work includes the investigation of the effect of O_3 addition on laminar flame speed (S_L) [11–15], flame stability [16,17], ignition delay [11,18–21], and emissions [18,22]. Nomaguchi and Koda studied the effect of O_3 addition on methane (CH_4) flame speed, S_L, at room temperature and pressure [11]. The flame cone-angle method was used with a circular nozzle burner. Their data showed that around 5000 ppm O_3 addition increased S_L by 5% at stoichiometric conditions and that the enhancement was greater for fuel-lean and fuel-rich cases. These observations were later supported by Halter et al. [12] with simulations and a similar experimental approach. A more recent experiment by Wang et al. [13] using the heat-flux burner showed a 3.5% increase in S_L with 3730 ppm O_3 addition at stoichiometric conditions, and 9% increase for 7000 ppm O_3. This trend agreed well with their simulation results. Another fuel, propane (C_3H_8), was investigated by Ombrello et al. [10,14]. A lifted laminar flame, in which liftoff height is very sensitive to S_L, was employed. When accounting for the kinetic and hydrodynamic effects, an approximately 4% enhancement of S_L at a stoichiometric condition was reported with 1260 ppm O_3 addition. Syngas has also attracted much attention. Approximately 9% enhancement to S_L was reported with 8500 ppm O_3 addition at stoichiometric conditions for a H_2/CO/N_2/air

mixture by Liang et al. [15]. O_3 addition can also improve flame stability. Recently, Vu et al. [16] demonstrated increased blowoff velocity and extended flammability limits in a Bunsen burner at atmospheric pressure using CH_4 and C_3H_8 as the fuels. With 3810 ppm O_3 addition, the enhancement of blowoff velocity at stoichiometric conditions was approximately 9% for CH_4 and 11% for C_3H_8 [16].

The effect of O_3 on ignition has also been investigated. Nomaguchi and Koda [11] demonstrated the effect of O_3 addition on accelerating spark ignition. The ignition delay time was investigated in terms of the minimum spark pulse duration for successful combustion in a spherical vessel. Two fuels, CH_4 and methanol (CH_3OH), were tested over a wide range of equivalence ratios (ϕ) at 20 and 24 kPa. It was found that when air was partially ozonized ($O_3/O_2 = 1\%$), the necessary ignition pulse duration was shortened significantly for both fuels. Similar phenomena at high pressure were then reported by Tachibana et al. [18] using a Cooperative Fuel Research (CFR) engine. They found that O_3 could decrease ignition delay time, equivalently increasing the effective cetane number. This finding inspired researchers to utilize O_3 to control the combustion process in homogeneous charge compression ignition (HCCI) engines [19–21]. Tachibana et al. [18] also reported that O_3 addition could increase nitrogen oxide (NO_x) concentrations but reduce carbon monoxide (CO), unburned hydrocarbons, and particle emission levels. Wilk et al. [22] observed the same trends in natural gas combustion using a modified Meker burner at room temperature and pressure.

The conventional understanding of these enhancements is that, due to its long lifetime, O_3 can be transported to the preheat zone and then decompose to release O atoms, which accelerate reactions by attacking fuel molecules [11,14]. A general observation from previous studies is that as one of the strongest oxidizers, O_3 always enhances combustion processes. However, this interpretation is based on the understanding that O atoms are always produced, which may not always be the case. It is possible that O_3 reacts with fuel before it decomposes to release O atoms. This process can be both beneficial and detrimental to enhancement. For example, in the ozonolysis process of hydrocarbons fuels

$$Fuel + O_3 = Products$$

there could be a dramatic difference in the behavior of saturated and unsaturated hydrocarbons [23]. Though there are disagreements among the measured kinetic data, the reaction between O_3 and CH_4 is very slow (reaction-rate constant of $k = 0.994$ cm^3/mole-s based on [24]) at room temperature and atmospheric pressure; however, the reaction between O_3 and ethylene (C_2H_4) is very rapid and even explosive [23,25] ($k = 1.12\times10^6$ cm^3/mole-s [26]) at the same conditions. Since C_2H_4 is an important intermediate [27] and a surrogate [28] species for jet fuels, a comprehensive understanding of its ozonolysis effect on flame propagation is important. Recent experiments [29] conducted at low pressures shows that S_L with C_2H_4-based flames were enhanced by O_3 addition. However in the 1950s, Gluckstein et al. [30] reported that the S_L of C_2H_4 was decreased by O_3 injection at room conditions. The contradictions of previous results raise the following question. Does O_3 always enhance flame propagation, and how does ozonolysis of fuels affect S_L at different pressures and temperatures? Glucksein et al. [30] suspected that the detrimental effect of O_3 addition was due to production of formaldehyde (CH_2O) from the reaction between O_3 and C_2H_4. This explanation may not be complete because (i) CH_2O has a greater effect on S_L than C_2H_4 and (ii) other reactive species such as H_2 could be formed by ozonolysis of C_2H_4 [31,32]. Replacing a portion of C_2H_4 by H_2 and CH_2O should have a positive effect on S_L. To the authors' knowledge, this is the only reference reporting a detrimental effect of O_3 on flame propagation. However, the uncertainty of the experimental data in this work is large, and the experiments may suffer from uncertain reactant composition. This is because a significant concentration of
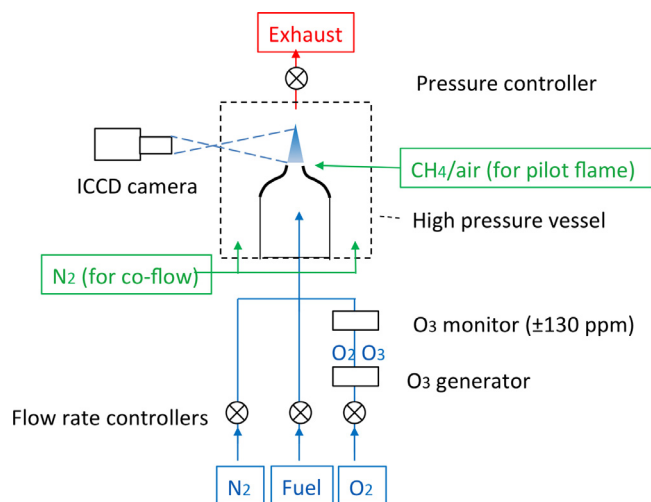

Fig. 1. Schematic of high-pressure Bunsen flame facility.

O_3 may have already been consumed before entering the flame zone due to the fast C_2H_4 ozonolysis reaction. Therefore, experiments with clear boundary conditions are necessary. In the present work, a low-temperature Bunsen burner is employed to "freeze" the ozonolysis reaction and thus minimize the O_3 consumption after the mixing process. Since the ozonolysis of C_2H_4 produces 1,2,3-trioxolane [33,34], which is pressure dependent, a low-pressure burner is employed to investigate the pressure effect of O_3 addition on the C_2H_4 flame.

Previously, all reported experiments on flame propagation enhancement by O_3 were conducted at or below atmospheric pressure and room temperature with little understanding of the operating conditions and fuel kinetics. Therefore, the goal of this work is to investigate the pressure dependence of the effect of O_3 addition on flame propagation speeds of various fuels.

2. Experimental and numerical methods

In this study, three experimental setups are employed to measure S_L: a high-pressure Bunsen flame facility [35,36], a low-pressure system, and a low-temperature system. The high-pressure facility is shown in Fig. 1. Axisymmetric Bunsen flames are produced with a contoured laminar nozzle, which is located in a pressure chamber with optical access for flame imaging. The high contraction ratio ensures that the exit velocity profile is uniform. The chamber is pressurized using a nitrogen (N_2) co-flow system and a throttled nozzle; it can operate at pressures up to 30 atm. Large-scale flow structures are removed before entering the converging nozzle by a combination of ball bearings and a ceramic flow straightener, which ensures laminar flow and a top-hat velocity profile at the exit, even at high flow rates. A sintered plate surrounding the nozzle exit produces a near-stoichiometric, flat, CH_4/air pilot flame, which helps in anchoring the flame at the high flow rates required for high pressure experiments. Chemiluminescence images of the Bunsen flame are acquired using an intensified charge-coupled device (ICCD) camera, and a gradient-based edge detection algorithm is used to determine the reaction zone location and thus calculate the flame area. The laminar flame speed (S_L) is calculated by dividing volumetric flow rate of the reactants, which is monitored using a bank of calibrated rotameters, by the flame area. This approach of using the reaction-zone-based flame area has been shown to produce accurate S_L because it can minimize flame curvature effects [36,37]. Employing high exit velocities and long flame lengths also helps to decrease the relative importance of the tip area and strain effects [36,38]. This experimental setup has been well validated for measuring S_L at high pressures for gaseous fuels in previous studies [35,36]. In the current setup,