

Gasoline Surrogate Combustion with Ozone Addition

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Abstract

In the present work, a numerical investigation on the laminar flame speed of Toluene Reference Fuel (TRF)/air/ozone mixtures has been carried out for different equivalence ratios, reactants temperatures and ozone concentrations. The 1-D numerical simulations have been performed with two modified chemical kinetic reaction mechanisms for TRF. The oxidative reactivity of the fuel has been improved thanks to the addition of ozone. Indeed, preliminary results show that ozone enhances the laminar flame speed and decreases the flame thickness of TRF/air mixture in the concentration range of 0-7000 ppm. For reactants temperature of 358 K at ambient pressure and for an ozone concentration of 7000 ppm, the increase in laminar flame speed is about 13% under lean conditions whereas it is about 4% under stoichiometric conditions. This work shows that the laminar flame speed is greatly influenced by ozone for unburned reactants temperatures greater than 550 K. Lean conditions enhance this behavior compared to the stoichiometric condition.

Introduction

The Laminar Flame Speed (LFS) is an important quantity to describe the reactivity, diffusivity and exothermicity of a fuel/air mixture. In combustion systems, LFS directly influences the combustion efficiency and pollutant emissions. In this context, the scientific research is focusing on the development of unconventional combustion strategies with the aim of reducing emissions and fuel consumption and increasing thermal efficiency. These strategies include the use of alternative fuels characterized by high LFS under lean conditions, and the use of standard fuel/air mixture enriched with either oxygen or chemical reactive species. Among them, ozone (O₃) is a promising chemical reactive species for increasing LFS, stabilizing the combustion variability, and controlling the ignition delay time. Indeed, the reaction $O_3 + N_2 \leftrightarrow O + O_2 + N_2$ plays a key role in the ozone decomposition for influencing LFS. Halter *et al.* [1] studied the role of ozone in methane/air combustion employing experimental and numerical approaches. The authors showed that, considering 2369 ppm of ozone at 300 K and 1 bar, LFS significantly increases and

the flame thickness decreases. Wang *et al.* [2] investigated the influence of different concentrations of ozone in the range 0-7000 ppm for the methane/air flames. They showed that LFS increases linearly with the ozone concentration. Furthermore, the highest increase has been observed for lean mixture conditions. Gao *et al.* [3] investigated, both experimentally and numerically, the influence of ozone on LFS of methane, propane, and ethylene. The results show that the LFS enhancement is more pronounced especially at high pressures. D'Amato *et al.* [4] numerically studied the influence of ozone on the methane/air for the ozone concentration in the range 0-7000 ppm. They confirmed that ozone addition improves LFS at high temperatures and pressures, and they extended these findings to an iso-octane/air mixture. In recent works, ozone has been employed to improve the thermal efficiency, emissions, and cycle-to-cycle variability of Spark-Ignition (SI) engines. Anaclerio *et al.* [5] proposed the use of ozone in SI engines fueled with gasoline/air/ozone mixtures under lean conditions. Their results indicated that ozone addition has a strong influence on the combustion process resulting in higher in-cylinder pressure with a reduction of burn delay, combustion phase and burn duration. In this work, a ternary mixture of iso-octane/n-heptane/toluene, named Toluene Reference Fuel (TRF) with 63/20/17 mol.% [6, 7] has been used as gasoline surrogate. A detailed kinetic mechanism for TRF with O₃ and a skeletal mechanism are proposed and validated to highlight the role of ozone on the LFS of commercial gasoline. The importance of the equivalence ratio and of the reactant temperature on the LFS is investigated and discussed for lean ($\phi = 0.6$) and stoichiometric conditions.

The Mathematical Model

Numerical simulations are carried out by using Cantera numerical code [8] to simulate adiabatic freely propagating laminar flames. The differential governing equations for one-dimensional premixed steady-state flame equations (state, mass continuity, species continuity, momentum and thermal energy equations) are solved. The initial gas temperature, pressure, and mixture composition are set. Two different reaction mechanisms for TRF with an ozone sub-mechanism [1] and Saxena NO_x sub-mechanism [9] are employed. Table 1 shows the number of species and reactions of each mechanism.

Table 1. Number of species and reactions of the TRF-O₃ detailed and skeletal mechanisms.

Mechanism	Type	Species	Reactions
Det TRF O ₃	Detailed	507	17860
Skel TRF O ₃	Skeletal	171	3535

Model Validation

The two reaction mechanisms have been validated (without ozone) against measurements for various equivalence ratios [15] and for mixtures of commercial

gasoline with air. The comparison is shown in Figure 1.a) [10-14] at 358 K and 1 bar and in Figure 1.b) at 373 K and 10 bar. Figure 1 shows that the numerical results are within the uncertainty range of the measurements. Furthermore, the figure shows that for rich mixtures ($\phi > 1.0$) higher LFS is found with the detailed mechanism. On the other hand, under lean conditions, the differences between the two mechanisms are negligible and are in fair agreement with the experimental data. To the best of the authors' knowledge, there are no data available in the literature for mixtures of gasoline with ozone.

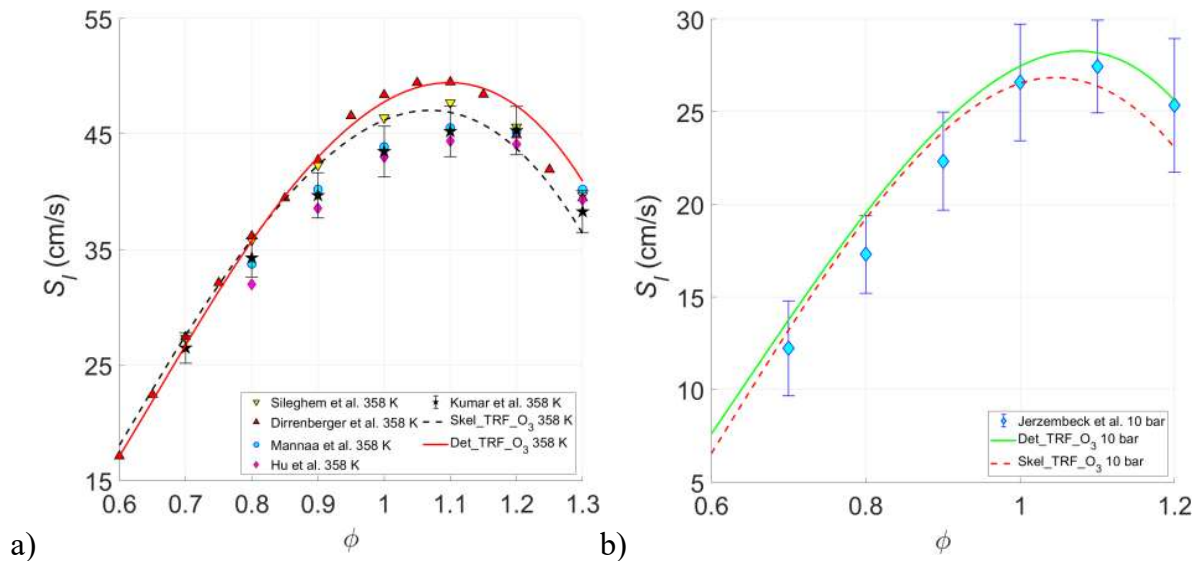


Figure 1. Gasoline/air mixtures at 358 K and 1 bar [10-14] (a) and 373 K and 10 bar [15] (b) for different equivalence ratios.

Results and Discussion

Firstly, the analysis has been carried out for TRF/air/ozone mixtures at 358 K and ambient pressure for two different ozone concentrations, i.e. 2330 ppm and 7000 ppm. Then, the influence of the reactants' temperature on the LFS has been discussed for both stoichiometric and lean conditions.

The influence of ozone

Figure 2.a) shows the laminar flame speed at 358 K and ambient pressure for different equivalence ratios and three ozone concentrations, i.e. 0, 2330 and 7000 ppm, by using the skeletal reaction mechanism. The enhancement of LFS has been defined as follows: $\varepsilon [\%] = (S_l - S_{l0})/S_{l0} \cdot 100$, where S_l and S_{l0} are the LFS with and without ozone, respectively. The results suggest that a) the presence of ozone increases the LFS across the entire set of equivalence ratios and b) the LFS increases more as the ozone concentration increases. Figure 2.b compares the percentage increase of LFS with the two chemical kinetic mechanisms. The highest LFS increase has been found for ultra-lean conditions ($\phi = 0.5$) and with 7000 ppm of ozone for both mechanisms. Specifically, such percentage increase is about 13.3%

and 11.8% for the detailed and skeletal mechanism, respectively. Furthermore, a gradual reduction of the LFS increase is observed as the equivalence ratio increases up to a minimum under about stoichiometric conditions for both kinetic mechanisms. Thereafter, LFS enhancement begins to increase again for slightly rich mixture conditions.

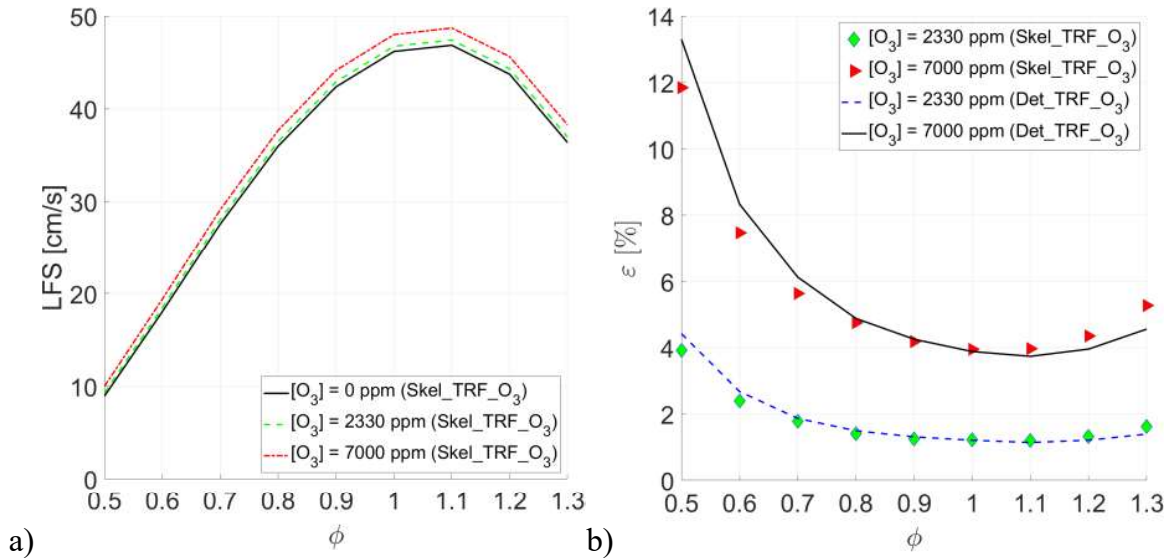


Figure 2. LFS of TRF/air without and with different ozone concentrations vs equivalence ratios at 358 K and 1 bar (a). LFS enhancement for different ozone concentrations for both skeletal and detailed chemical kinetic mechanisms (b).

Under lean conditions ($\phi = 0.6$), the burnt gas temperature increases by 8.5% with an increase of 6.7%, 5.2%, 7.9% and 16.7% of the mole fractions of O, OH, H and HO₂, respectively. Under the same lean conditions, the flame thickness, defined as $\delta_l = (T_{max} - T_{min}) / \max(\nabla T)$, is 0.70 mm for the TRF/air flame without ozone and decreases to 0.68 mm when 7000 ppm of ozone is added to the mixture.

The influence of temperature

Several unburned mixture temperatures, ranging from 358 K to 700 K, for ozone concentrations of 0, 2330 and 7000 ppm at 1 bar have been considered. Figures 5.a) shows the LFS as a function of the unburned gas temperature for different ozone concentrations under stoichiometric and lean conditions ($\phi = 0.6$). Figures 5.b) gives the LFS slope with respect to the unburned temperature ($dS(T)/dT$). The LFS of the mixture without ozone smoothly increases with the temperature for both stoichiometric and lean conditions. On the other hand, the presence of ozone in the mixture significantly influences the LFS for temperatures higher than 550 K. Indeed, Figure 5.b) shows that the LFS variation with ozone increases linearly up to about 475 K for both stoichiometric and lean mixture conditions. For higher temperatures, the LFS slope starts to increase significantly until it reaches a maximum at about 600 K. The results show that for both ozone concentrations, i.e. 2330 ppm and 7000 ppm, an unburned gas temperature of about 550 K represents the threshold beyond which ozone strongly influences the oxidation mechanism of TRF.

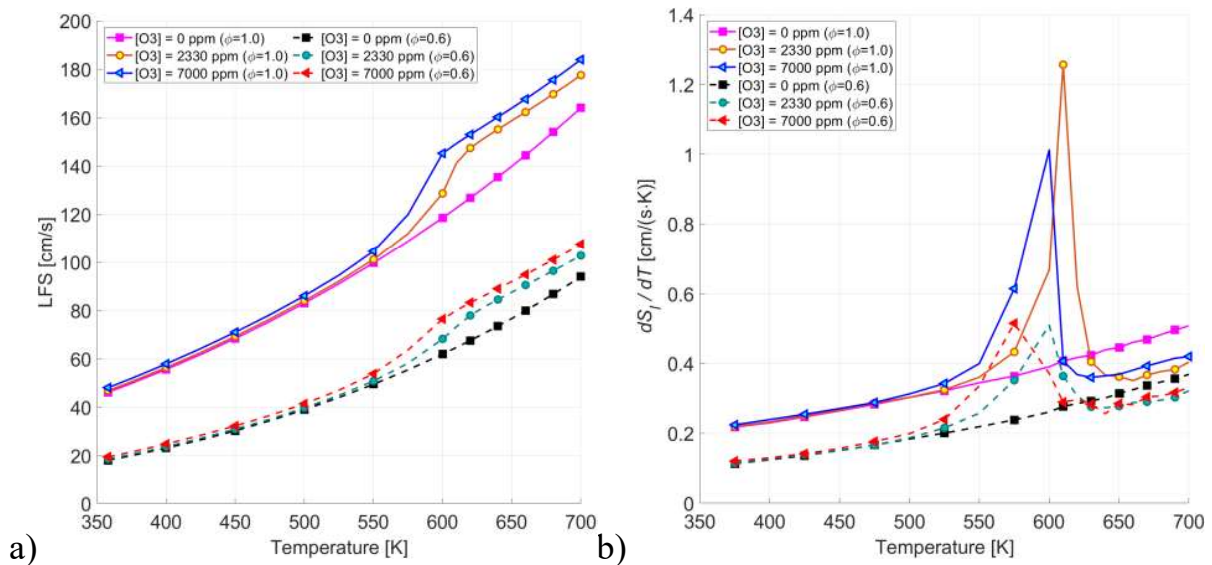


Figure 5. LFS of TRF/air/O₃ mixtures (a) and LFS slope (b) vs unburned mixture temperature under stoichiometric and lean conditions at ambient pressure (1 bar).

Conclusions

In this work, the influence of ozone addition on the combustion of TRF/air flames has been investigated. One-dimensional numerical simulations have been performed to compute the laminar flame speed by using two chemical kinetic mechanisms, detailed vs skeletal.

The results can be summarized as follow:

- under lean conditions ($\phi = 0.5$), at 358 K and 1 bar, the presence of ozone in the TRF/air mixture increases the laminar flame speed of about 13%, whereas under stoichiometric conditions, such increase is about 4%;
- under lean conditions, the presence of ozone favors the increase of the main radicals and the reduction of the flame thickness;
- the influence of ozone becomes more relevant at high reactants temperatures, showing a sharp increase in the laminar flame speed over 550 K.

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