The Effect of Nitrates on Deflagration to Detonation Transition

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Introduction

The present paper investigates the effects of Nitrogen Dioxide (NO_2) on the run-up distance for deflagration to detonation transition in propane-O_2-N_2 mixtures. Renewed interest in pulse detonation engines has focused attention on the deflagration to detonation transition (DDT) problem. Direct initiation of detonation in fuels of practical interest for propulsion applications would require charges on the order of ~100 g of high explosive for each cycle of initiation. Other initiation sources (sparks, lasers, etc.) cannot easily provide this amount of energy (~100-1000 kJ) on a cyclic basis. On the other hand, the usual path of "self initiation", namely DDT, typically requires a run-up distance of 10 or more tube diameters in the fuels of interest, characterized by cell size $\lambda \approx 5$ cm. A means of rapidly effecting initiation through DDT is therefore sought.

Significant work has been carried out in diesel combustion research, and a number of nitrate-based compounds (isopropyl nitrate, ethylhexyl nitrate, etc.) have been found to sensitize diesel fuels. This sensitization is generally quantified by a measure of the reduction in ignition delay. The common view regarding the mechanism by which these sensitizers operate is that they decompose to form NO_2, which readily reacts with methyl radicals in the combustion zone. The purpose of this investigation is to determine if this chemical kinetic effect reduces the run-up distance in the mixtures of interest.

The run-up distance (RUD) to detonation is governed by the transition through a series of propagation mechanisms. The early stages of laminar flame instability, and transition to turbulence are controlled by fluid dynamic processes. These processes are expected to be only weakly dependant on chemical kinetics. However, during the shock-induced chemistry and intense mixing of the final stages of DDT, propagation and transition should be dominated by kinetic rates. Indeed, the RUD is known to reduce with the detonation cell size, indicating that kinetic rates play a significant role in DDT.

In the present study, direct addition of NO_2, which reacts with methyl radicals as described above, is used to determine the effect of modifying the kinetic rates. Specifically, the current study quantifies the effect of NO_2 addition on the run-up distance of propane (C_3H_8)-O_2-N_2 mixtures. Propane was selected as a simulant for the vapor phase of liquid fuels such as Jet-A and JP-10, since they have similar sensitivity as determined by measurements of detonation cell size.[1]

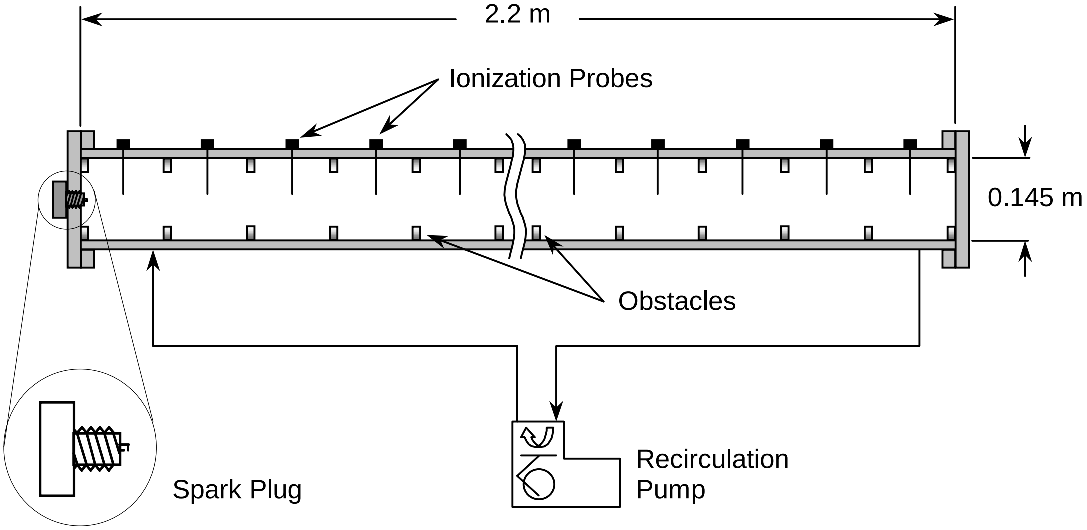

Fig. 1 Schematic of experimental setup.

Experimental Details

The experimental work was carried out in a 2.2 m long, 14.5 cm internal diameter steel tube, which was closed at both ends. The tube was lined with an obstacle array of orifice plates with blockage ratio BR = 0.43 (43% blocked area, corresponding to an obstacle plate internal diameter of 10.9 cm) and spaced one tube diameter apart. A schematic representation of the apparatus is shown in Fig. 1. The role of these obstacles is to promote the onset of turbulence, and the intensity of the subsequent turbulent mixing responsible for the initial phases of flame acceleration, prior to DDT. The blockage ratio and spacing used are based on prior results obtained at McGill by Peraldi et al. [2], which indicate this to be a near optimum configuration. These previous experiments have also shown that the presence of obstacles reduces the scatter in run-up distance measurements obtained in smooth-wall tubes. Indeed, the results presented here show very reproducible results for a given set of initial conditions.

Experiments were carried out using mixtures of C_3H_8-O_2-N_2 in order to establish a baseline run-up distance. Then, experiments were conducted with NO_2 added to the baseline mixture, and finally, with O_2 added to the baseline mixture in the proportion necessary to achieve the same stoichiometry as that of the NO_2 experiments. This last set of experiments served to isolate the energetic effect of NO_2 from the kinetic effect. The experimental sequence began by flushing the chamber with shop air from a high-pressure line, and then evacuating the chamber through a vacuum pump to less than 1 kPa. The gas mixture was prepared by injection to the required partial pressure of each constituent gas, with a final pressure of 103 kPa for all the experiments. Mixing was achieved by recirculating the gas through a bellows-type recirculation pump, and an automotive spark plug was used to ignite the mixture at one end of the vessel. Time-of-arrival measurements were made with ionization probes spaced roughly every tube diameter along the length of the tube. The probe signals were recorded on digital Lecroy oscilloscopes. The apparatus as described permits determination of the velocity profile of the combustion wave and the location of onset of detonation to within one tube diameter for the mixtures studied.

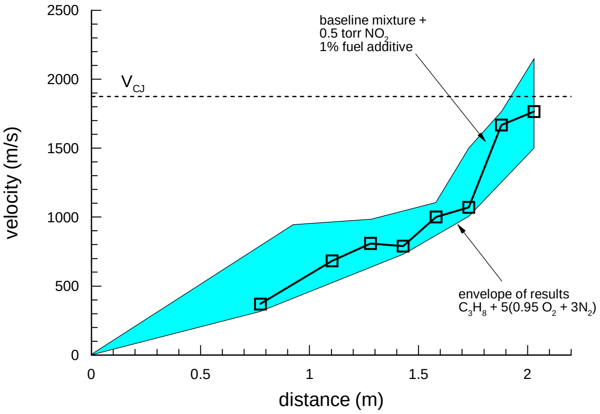

Fig. 2 *V*-*x* diagram of flame trajectory for 1% NO_2 addition.

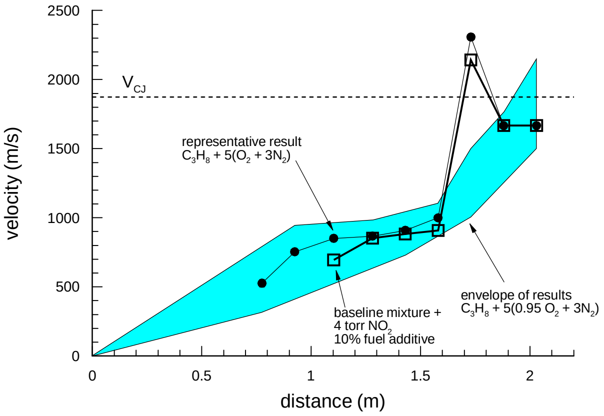

Fig. 3 *V*-*x* diagram of flame trajectory for 10% NO_2 addition and stoichiometric mixture.

Results and Discussion

The primary result of interest in these experiments is the run-up distance, i.e. the distance from ignition to onset of detonation. It should be noted that, due to the presence of obstacles, the detonations reported here display velocities below the Chapman-Jouguet velocity. This is in agreement with previous studies of detonation propagation in very rough tubes by Shchelkin [3], Guenoch and Manson [4], Brochet [5], and more recently, Lee et al. [6], and Knystautas et al. [7], which have shown velocity deficits of up to 50% of the C-J velocity. These detonations exhibiting velocity deficits are called quasi-detonations. Since we are interested in the transition to detonation, and not in the specifics of the final propagation regime, no distinction is made between quasi-detonations and detonations in this study. The location of onset of detonation is indicated by a sudden transition to propagation velocities of the order of 1500 m/s.

Figure 2 shows a shaded envelope representing the results from six experiments in a control mixture of C_3H_8-O_2-N_2, which was slightly fuel rich ($\phi = 1.05$). The graph represents the velocity of the combustion front as measured by ionization probes along the length of the tube. The dashed line represents the C-J velocity for these mixtures and is used as a reference for determining transition to detonation. It is seen that the baseline mixture reproducibly exhibited transition to detonation within a distance of 2 m from the point of ignition. Experiments were then performed with the same baseline mixture to which was added 0.067 kPa (0.5 Torr) of NO_2, corresponding to a 1% fuel additive. A typical result is also shown in Fig. 2 The velocity profile lies entirely within the control envelope, indicating that there is no detectable effect in flame acceleration or onset of DDT with this small addition of NO_2.

Further experiments involved the same baseline mixture, to which was added 0.533 kPa (4.0 Torr) of NO_2, corresponding to a 10% fuel additive. A typical result is shown in Fig. 3, along with the previous control envelope. From this result, two conclusions can be reached. On one hand, it is clear that the NO_2 addition has shortened the RUD by two tube diameters, corresponding to a 15% reduction, which is the primary effect of interest. On the other hand, we see that the turbulent flame acceleration prior to the onset of DDT remains within the control envelope. This is in agreement with the mechanism of turbulent flame acceleration, which is dominated by fluid mechanic effects. In order to establish whether the NO_2 effect is a kinetic one as proposed earlier, or simply an energetic effect resulting from the simple addition of oxidizer, a number of experiments were conducted with the control mixture to which was added 0.93 kPa (7.0 Torr) of O_2. A typical result is shown in Fig. 3, and indicates a velocity profile and a detonation onset in close agreement with that of the NO_2 sensitized mixture. If we take into account the fact that gaseous NO_2, under the experimental conditions of 293 K and 1 atm, polymerizes into roughly 70% N_2O_4 and 30% NO_2 [8], we see that both the NO_2-sensitized and the O_2-sensitized experiments contain roughly the same amount of additional O_2. This implies that the observed effect is in fact an energetic one: the additional NO_2 acts simply as an oxidizing agent. The chain branching mechanism that was proposed for the NO_2 sensitized mixture does not exhibit a significant effect on the transition to detonation in these experiments.

Conclusions

The experiments carried out have allowed the measurement of run-up distance within an accuracy of 1 tube diameter in C_3H_8-O_2-N_2 mixtures with and without NO_2 sensitization. The results indicate that, at 293 K, and 1 atm, a small amount of NO_2 (1% fuel additive) has no discernible effect on DDT. A larger amount of NO_2 (10% fuel additive) resulted in a 15% reduction in run-up distance, but the same effect was achieved by adding roughly the same amount of pure oxygen as that supplied by the NO_2. These results imply that the effect of NO_2 is an energetic one, rather than a chemical kinetic effect resulting from the reaction of NO_2 with methyl radicals.

It is also interesting to note that in all cases, the flame acceleration up to speeds just under 1000 m/s lies within the same envelope. This confirms the proposed model of flame acceleration through turbulent mixing, and also highlights the fact that the effects of chemical sensitizers are confined to that region just prior to the onset of DDT when the mixing becomes very intense and shock induced chemistry becomes possible. Since the initial stages of flame acceleration generally occupy the longest distance when ignition is effected via a weak spark, the resolution within the area of interest for chemical sensitization is minimal with respect to the scale of DDT. It therefore seems that an effective way of promoting DDT would require first a method for promoting the initial conditions required for the chemical sensitizers to become effective.

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