The Effects of Chemical Sensitization on Deflagration to Detonation Transition

by

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Abstract

Renewed interest in pulse detonation engines has focused attention on the problem of deflagration to detonation transition (DDT) in fuel-air mixtures. A prohibitively large deposition of energy is required for direct initiation of higher-hydrocarbon fuels in air. Consequently, methods are being sought to reduce the run-up distance required for DDT. It has been proposed that the addition of a very sensitive fuel, or of nitrate-based sensitizers typically used in diesel fuels, could increase the sensitivity of hydrocarbon fuel-air mixtures by increasing the chemical kinetic rates. Studies have indicated that the effect of nitrates on diesel fuels occurs through the action of nitrogen dioxide (NO_2) abstracted from the nitrate molecule.

Experiments were therefore carried out in order to evaluate the effect of acetylene (C_2H_2) and NO_2 addition to propane (C_3H_8) – oxygen (O_2) – nitrogen (N_2) mixtures at ambient conditions. The run-up distance for mixtures of $C_3H_8/C_2H_2 - O_2 - N_2$ was first investigated for varying proportions of C_3H_8 and C_2H_2 in the fuel. Then, the run-up distance and detonation cell size were established for $C_3H_8 - O_2 - N_2$ mixtures without NO_2 and with NO_2 added as a 10% to 50% fuel additive. The results show that the effect of C_2H_2 is a very gradual reduction in run-up distance with increasing C_2H_2 concentration, making it an ineffective additive. The addition of NO_2 causes no change in either the run-up distance or the cell width, indicating that the kinetic changes brought about by the NO_2 are not significant to the initiation of detonation. This result is shown to agree with kinetic models that suggest that NO_2 is not very effective at promoting ignition at very high temperatures such as that characteristic of detonations.

Résumé

Les efforts récents pour développer un moteur à détonation, dit *pulse detonation engine* (PDE) a mené à un intérêt accru pour le problème de la transition déflagration-détonation (DDT) dans les mélanges carburant-air. Un dépôt d'énergie excessif est nécessaire pour le déclenchement direct d'une détonation dans ces mélanges. En conséquence, des méthodes sont recherchées pour réduire la distance nécessaire pour la DDT (distance de transition). Certains chercheurs ont proposé que l'ajout de sensibilisateurs, tel qu'un carburant très sensible ou un nitrate typiquement utilisé dans les carburants diesel, pourrait augmenter la sensibilité des mélanges hydrocarbure-air en accélérant la cinétique chimique. Des études ont indiqué que l'effet des nitrates sur le délai d'allumage des carburants diesel résulte de l'action du bioxyde d'azote (NO_2) libéré par la molécule de nitrate.

Des expériences furent donc effectuées afin d'évaluer l'effet de l'acétylène (C_2H_2) et du NO_2 dans des mélanges de propane (C_3H_8) – oxygène (O_2) – azote (N_2) a 293 K et 100 kPa. La distance de transition pour des mélanges $C_3H_8/C_2H_2 - O_2 - N_2$ avec différentes proportions de C_3H_8 et de C_2H_2 dans le carburant fut étudiée. Puis, la distance de transition, et la largeur des cellules de détonation furent établies pour des mélanges de $C_3H_8 - O_2 - N_2$ sans NO_2 et avec du NO_2 selon une proportion de 10% à 50% d'additif au carburant. Les résultats indiquent que l'effet de C_2H_2 est une réduction graduelle de la distance de transition à mesure que la concentration de C_2H_2 augmente, et qu'il n'y a aucun effet, ni sur la distance de transition, ni sur la largeur des cellules suite a l'ajout du NO_2. Il apparaît donc que le C_2H_2 n'est pas un additif efficace et que les effets cinétiques provoqués par le NO_2 n'affectent pas le déclenchement de la détonation. Ce dernier résultat est conforme aux modèles cinétiques qui suggèrent que le NO_2 ne favorise pas l'allumage à température très élevée comme celle caractéristique des détonations.

Acknowledgements

Returning to school after working in industry for over three years was difficult at first... luckily, I found what I was looking for: questions.

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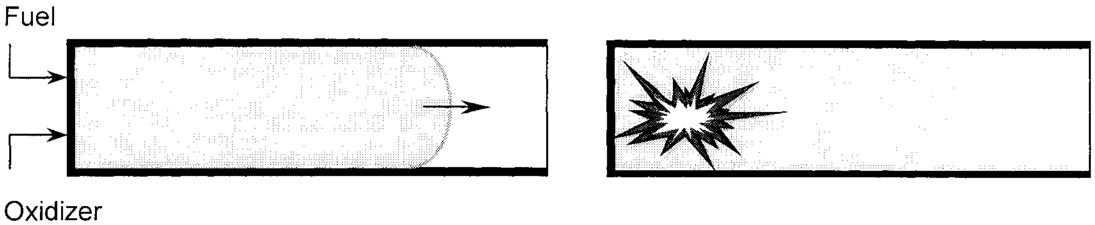
Chapter 1 Introduction

1.1 Background

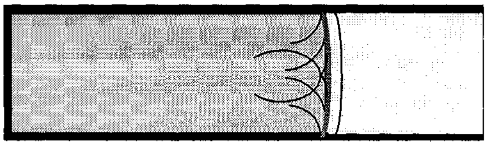
1.1.1 The Pulse Detonation Engine

The problem of deflagration to detonation transition (DDT) has been the subject of renewed attention in the past years. This is in large part due to the emergence of the pulse detonation engine (PDE) as a propulsion concept offering the possibility of high efficiency and low mechanical complexity as compared to a turbojet engine. The PDE is an unsteady propulsive device, operating in a cyclic manner to generate impulsive thrust [1,2]. A schematic representation of a simple PDE at various phases of its cycle is shown in Fig. 1.1. The cycle starts with the injection of an explosive mixture into the combustion chamber (Fig. 1.1a). A detonation is then initiated in the mixture (Fig. 1.1b), and propagates through the chamber (Fig. 1.1c). Detonative combustion is characterized by auto-ignition of the reactant gases behind a strong shock wave. The shock wave serves to bring the reactants to the critical conditions for auto-ignition, while the energy released by the combustion supports the leading shock. The jet of hot, high-pressure combustion products exiting the chamber behind the detonation creates a pulse of thrust (Fig. 1.1d). The chamber is then filled again to start a new cycle. A quasi-steady level of thrust can be achieved by repeating this sequence at a sufficiently high frequency.

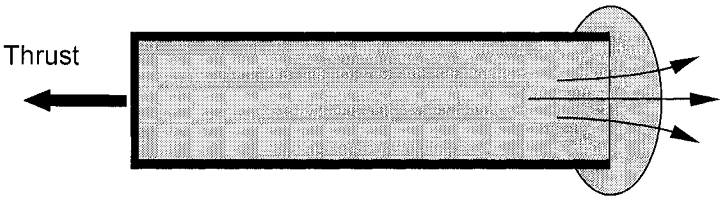
The PDE concept dates back over 50 years [3,4], however, a number of significant scientific and technical challenges made PDE development unfeasible at the time. With improved understanding of detonation phenomena, we are now in a better position to address the issues related to combustion. Of particular interest is the challenge in finding a path to achieve detonation in relatively insensitive fuel-air mixtures within the limited size of the chamber. This issue, which involves the understanding of detonation initiation and propagation and, in particular, the dominating factors governing deflagration to detonation transition, is addressed in this thesis.



a- Injection b- Initiation



c- Propagation



d- Exhaust

Fig. 1.1 Simplified PDE cycle

1.1.2 Detonation Initiation

It is generally recognized that there are two ways of initiating a detonation: *direct initiation* and *deflagration to detonation transition* (DDT). A review of both of these mechanisms can be found in Lee [5] and in Shepherd and Lee [6]. Direct initiation results in the "instantaneous" formation of a detonation. This is achieved by the localized deposition of a large amount of energy, resulting in a blast wave of sufficient strength and duration to initiate detonative combustion. The minimum energy required to achieve direct initiation is known as the *critical energy*. If the energy of the source is lower than the critical energy for a given mixture, the reaction zone decouples from the blast and decays to a low-speed flame.

In DDT, a relatively low energy source is used to ignite a flame. Under the appropriate conditions, the flame may accelerate and undergo a transition to detonation. The distance required for this process is called the *run-up distance*. DDT involves propagation speeds

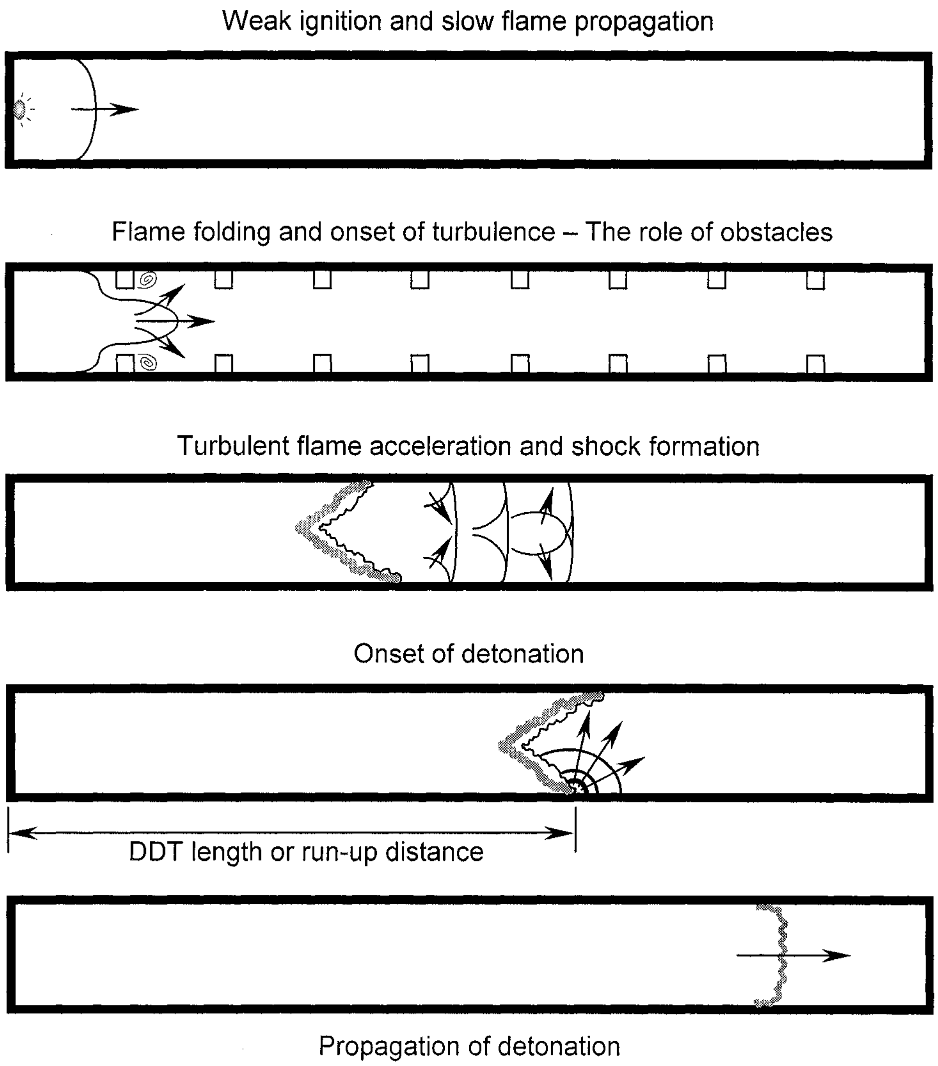


Fig. 1.2 Schematic illustrating the sequence of events for DDT

ranging from tens of centimetres per second for laminar hydrocarbon-air flames to around 2 km/s for a steady detonation. This apparent acceleration is more correctly interpreted as a series of transitions to gradually faster propagation mechanisms. The propagation velocity is a reflection of the speed at which each mechanism is able to "process" or burn each subsequent layer of gas.

The sequence of propagation mechanisms is represented graphically in Fig. 1.2. The growth of the initial flame kernel and its propagation as a laminar flame is governed by the diffusion rates of heat and free radicals to the layer of unburned gas ahead of the flame. In a closed-end tube, a number of mechanisms are then responsible for the transition to turbulent flame propagation and the subsequent turbulent flame acceleration. The first mechanism is due to flame instabilities (e.g., Rayleigh-Taylor), which contribute to wrinkle the surface of the flame, thus increasing the flame area. This increases the volumetric burning rate and results in an increase of the propagation velocity.

A more significant mechanism results from the turbulent flow created ahead of the flame by the expansion of the combustion products. When the flame propagates into this turbulent flow, the subsequent folding of the flame sheet results in a significant increase in the burning area and the rapid mixing of burnt products with the fresh mixture. The result is a fluid dynamic feedback mechanism whereby the turbulent flow created by the flame leads to a higher burning velocity, which in turn leads to increased turbulence. It is of particular interest to note that using obstacles in the path of the flame can enhance this effect. The obstacles act to fold the flame and create vortex structures, leading to rapid mixing. Observations by Laffitte [7] and Shchelkin [8] demonstrated that a drastic reduction in run-up distance could be obtained by artificially roughening the tube walls. The mechanisms responsible for this phenomenon have been studied by Moen *et al.* [9], and a review of the propagation mechanisms and the importance of turbulence in creating the necessary conditions for the initiation of detonation can be found in Lee and Moen [10].

As the turbulent flame reaches velocities of the order of 1000 m/s, the compression waves eventually coalesce into a shock, which generates sufficient adiabatic compression to initiate chemical reactions. At this point, the stage is set for the onset of detonation. With the critical conditions in place, the actual detonation wave generally results from the growth of a localized explosion in the turbulent flame – shock complex (Urtiew & Oppenheim [11]). This explosion, or small blast, rapidly overtakes the leading shock and propagates as a self-sustained detonation. Moen *et al.* [9] have identified another mechanism whereby the detonation is initiated by the progressive amplification of pressure waves traversing the reaction zone in the final stage of DDT. In all cases, it appears that the final onset of detonation is the result of a rapid wave amplification process, which occurs once the gases have reached a certain critical state.

1.1.3 Issues Regarding Detonation Initiation in a PDE

The two initiation mechanisms described above point to two methods to achieve a detonation in a PDE. The use of direct initiation requires an igniter capable of generating a blast of sufficient strength to initiate a self-sustained detonation and a means to repeat this blast initiation tens to hundreds of times per second. The critical energy to directly initiate a stoichiometric mixture of propane – air is over 280 kJ [12]. Therefore, considering the energy released in detonating a typical high explosive (5.41 kJ/g of TNT) [13], the energy required corresponds to a ~ 50 g charge per cycle. This is clearly an impractical solution. Alternative initiation sources such as sparks or lasers cannot easily produce the required 100's of kilojoules per cycle. For this reason, DDT appears to be the more viable solution to detonation initiation in a PDE. However, the typical dimensions quoted for a PDE (~ 1 m length and ~ 0.1 m internal diameter) and the requirement for the use of a low sensitivity jet fuel such as JP-10 ($C_{10}H_{16}$) are major hurdles in achieving DDT at all.

JP-10 is a low vapour-pressure jet fuel, currently used in gas turbine engine combustors in liquid spray form. The task of achieving DDT in a fuel-air spray has been addressed by a number of researchers (Dabora *et al.* [14], Bar-Or *et al.* [15,16], Lin *et al.* [17], Papavassiliou *et al.* [18]). It is clear from these studies that low vapour pressure sprays are more difficult to detonate than a pure vapour. The general consensus is that the distance required for DDT in a spray is prohibitive and current PDE programs are generally seeking ways to pre-vaporize the fuel. The sensitivity to detonation of JP-10 vapour has been shown to be similar to that of gaseous hydrocarbons, such as propane (C_3H_8) (Akbar *et al.* [19]). However, even with such gaseous hydrocarbon fuels in air, the distance required for DDT, or *run-up distance*, is prohibitively long in a smooth tube. Obstacles can be used to drastically reduce the run-up distance, but this is at the expense of heat and momentum losses, resulting in reduced thrust efficiency. Cooper *et al.* [20] found a 25% reduction in impulse with orifice plate obstacles lining the tube. Therefore, the principal hurdle to achieving detonation for PDE's is finding a way to reduce the run-up distance by an order of magnitude with minimal loss of efficiency. A two-step procedure may be optimal. Some mechanical means such as obstacles could be optimized to generate a high-speed turbulent deflagration, while a chemical sensitizer could assist in the final stages of DDT.

Lee's [5] analysis of the mechanisms for direct initiation and DDT, as well as some more recent work [21,22], relate the critical energy for direct initiation to the chemical energy contained in the mixture within one or two detonation cell lengths. These studies indicate that the chemical energy available within one or two cell lengths matches the energy released in a detonation kernel of sufficient strength for direct initiation. While the typical cell size for fuels such as JP-10 or C_3H_8 is of the order of 5 cm, the run-up distance for these fuels in air is easily over 10 tube diameters (assuming a 10 cm diameter tube). The fact that the energy required for detonation initiation is contained within the first tube diameter implies that drastic reductions in run-up distance could be achieved if a mechanism for rapidly achieving the critical onset conditions is identified.

1.2 Evaluating Fuel Sensitivity

The sensitivity of a fuel is often evaluated by measuring its *induction time* [23] (i.e. the time required for significant energy release to start at a given temperature). This is typically done by injecting a mixture in a shock tube and processing it with a shock of known strength. Then the occurrence of a sharp pressure rise, or a jump in concentration of certain radicals, such as OH, is monitored. A certain threshold level is taken to indicate that ignition has occurred. The shorter the induction time, the more sensitive the fuel. In a detonation, the induction time translates into a characteristic distance between the leading shock and the beginning of significant energy release, called the *induction zone length.*

For detonation studies, the cell width is often used as a measure of sensitivity. A review of the characterization of a detonable mixture by cell size can be found in Lee [24]. The cellular pattern of a detonation can be observed by placing a soot-coated foil or plate along the path of the detonation. The intersecting shocks in the detonation front trace out the cells in the soot, which can then be easily measured. Shchelkin and Troshin [25] first proposed that these cells were representative of the sensitivity of the mixture. Westbrook and Urtiew [26] proposed simple linear correlations between the induction zone length in a one-dimensional detonation model and the experimental cell size. More thorough analysis has shown that these correlations are very approximate, as argued by Shepherd [27] and Gavrikov *et al.* [28]. Nevertheless, the fact remains that there is proportionality between the sensitivity of a mixture and its cell size.

The use of run-up distance as a measure of sensitivity in this study was motivated by the current interest in PDE's. It is clear from the previous discussion that this is the parameter of choice for PDE's. Furthermore, it is known that the run-up distance of a mixture relates to its cell size. This is illustrated by initial experiments carried out in mixtures of acetylene (C_2H_2) – oxygen (O_2) – nitrogen (N_2), and propane (C_3H_8) – O_2 – N_2 (Table 1.1). These were done in a 0.145 m diameter steel tube lined with obstacles resulting in a 43 % area blockage. The details of the experimental apparatus are given in Chapter 2. The results for stoichiometric mixtures with an N_2 to O_2 molar ratio of 3.0 (lines 1 and 2) show that the acetylene mixture detonates within 0.8 m, while the propane mixture requires more than twice the distance. The corresponding cell sizes are 7-8 mm for C_2H_2 [29, 30], and 30 mm for C_3H_8 [29], indicating that the run-up distance increases as the mixture sensitivity decreases. Furthermore, if the N_2 dilution in the C_3H_8 mixture is decreased so the cell size becomes ~ 8 mm [29] (line 3), the run-up distance becomes identical to that of the acetylene mixture with the same cell size. Run-up distance was therefore used throughout this investigation, and cell size measurements taken only to confirm the sensitivity variations revealed by the run-up distance measurements.

	N_2/O_2	λ (mm)	RUD (m)
C_2H_2	3.0	7-8	0.8
C_3H_8	3.0	30	2.0
C_3H_8	1.4	8	0.8

Table 1.1: Cell size variation with N_2 dilution and run-up distance in a 0.145 m diameter tube with 43 % blocked area (all mixtures stoichiometric)

1.3 Chemical Sensitization

Since the run-up distance and cell size of a fuel are clearly linked to its induction delay, it has been proposed that the use of chemical additives capable of reducing the induction delay could lead to a reduction in run-up distance. The most straightforward additive is a more sensitive fuel. Previous work (Westbrook & Haselman [31]) suggests that the addition of a small amount of ethane in methane can significantly reduce its ignition delay. With this in mind, it has been suggested that acetylene (C_2H_2), the most sensitive hydrocarbon fuel, could be added to JP-10 to increase its sensitivity [32]. As seen in Table 1.1, the cell size of C_2H_2 is significantly less than that of C_3H_8. In the ideal scenario, a small amount of C_2H_2 added to the base fuel would significantly increase its sensitivity.

The use of various other additives has been motivated by work with chemical additives in diesel fuels. Difficulties related to ignition, coupled with the widespread use of diesel fuels in industrial and military applications, have led to the development of very efficient fuel additives, primarily nitrates and peroxides. A typical example is given in Clothier *et al.* [33] where an addition of 1% 2-ethylhexyl nitrate (2-EHN, also called iso-octyl nitrate) reduced the ignition delay of diesel fuel by 34% (from 7.4 ms to 4.9 ms) for given experimental conditions. A review of the effectiveness of various sensitizers, including 26 nitrates and 9 peroxides can be found in Robbins *et al.* [34]. These studies show that nitrates and peroxides significantly affect the ignition kinetics of diesel fuels. It appears as though nitrates lead directly to rapid ignition paths, while peroxides are scavengers of sulphur and nitrogen containing compounds that tend to inhibit ignition.

With the growing interest in detonation and supersonic combustion for propulsion applications, it has been proposed that nitrates may result in analogous sensitizing effects for hydrocarbon fuels. Davidson *et al.* [35] reported a small change in the induction delay when he added 180 ppm of 2-EHN in n-heptane/O_2/Ar. Sidhu *et al.* [36] used 1% 2-EHN in JP-7 and JP-8 and reported 5% to 20% reductions in induction delay. While it appears clear that nitrates are effective in reducing the induction delay of some hydrocarbon fuels, the path for this reduction is unclear. This point is brought out clearly by the work of Zhang *et al.* [37] who studied the effect of iso-propyl nitrate (IPN) on the detonation sensitivity of hexane. They demonstrated that the detonation cell width of hexane-IPN-air mixtures decreased as the IPN concentration increased. However, to achieve a 50% reduction in cell width, approximately equal amounts of IPN and hexane were required. The substantial amount of IPN present resulted in an increase in the CJ velocity, indicating an alteration of the energetics of the mixture. IPN cannot be considered a sensitizer in this case since sensitization should require only a small amount of the additive, affecting the ignition kinetics without modifying the energetics of the mixture. Another such result was given by Frolov *et al.* [38]. They computed the effect of adding hydrogen peroxide (H_2O_2) to stoichiometric mixtures of iso-octane – air, and n-heptane – air. For a 10% overall content of H_2O_2, they found that the cell size decreased tenfold. Again, this cannot be considered as a sensitizing effect since there is on the order of ten times as much additive as fuel in these mixtures.

1.4 Outline of the Present Work

In this study, the effect of C_2H_2 and NO_2 on hydrocarbon fuel detonations was investigated experimentally. The effect of acetylene was evaluated by measuring the run-up distance for fuel compositions of C_3H_8 and C_2H_2 in various proportions. For acetylene to be considered an effective fuel additive it should cause a sharp reduction in run-up distance at low concentrations. Indeed, for practical reasons an additive should only be required as a small percentage of the total fuel requirement.

In the case of NO_2 addition, particular attention was paid to kinetic effects by comparing the run-up distance for $C_3H_8 – O_2 – N_2$ mixtures both with and without NO_2 addition, but with identical energetics. NO_2 was chosen as the candidate sensitizer to simplify the nitrate chemistry to a minimum and because, contrary to most nitrate compounds, NO_2 can be used in vapour form under the experimental conditions studied. Furthermore, work by Slutskii [39] has indicated that the effect of nitrate promoters on ignition delay is a result of the NO_2 generated by nitrate decomposition. He suggested that NO_2 reduces induction time by leading to a CH_3 oxidation channel. CH_3 radicals are present in the oxidation reactions of all hydrocarbons and tend to inhibit high temperature ignition (defined as approximately ≥ 1200 K) by recombining, resulting in chain termination (Westbrook [40]):

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (1.1)$$

A rapid oxidation path for CH_3 should therefore accelerate ignition kinetics. Work by Zaslonko *et al.* [41, 42] has shown that there is indeed a very high yield of NO_2 from the thermal decomposition of nitrates. In the experiments by Clothier *et al.* [33], the effectiveness of EHN as an additive to diesel fuel was compared to that of injecting NO_2 gas in the combustion chamber. They demonstrated an equivalent effect, confirming the hypothesis that EHN acts through its decomposition product: NO_2. In the early study by Norrish and Wallace [43], it was shown that NO_2 reduces the ignition temperature of CH_4-O_2. They proposed that NO_2 results in a path for creation of O atoms. More recently, Dorko *et al.* [44] demonstrated important reductions in ignition delay of CH_4-O_2 when part of the O_2 was replaced with NO_2. Dabora [45] noted 30%-50% reductions in ignition delay with 1%-2% addition of NO_2 to CH_4-air at high temperature (1300 – 1800 K) and pressure ($\approx$ 14 atm), corresponding closely to post-shock detonation conditions. While there is clear evidence that NO_2 has an effect on both diesel and hydrocarbon fuels, the nature of that effect is unclear. Furthermore, with the exception of Dabora [45], the effect was generally demonstrated at ignition temperatures below those typical of detonations. It is, therefore, of interest to identify the specific role of NO_2 in hydrocarbon detonations.

Chapter 2 Experimental Details and Procedure

2.1 Overview

A detonation tube was used to measure the run-up distance to detonation in mixtures of propane (C_3H_8) / acetylene (C_2H_2) – oxygen (O_2) – nitrogen (N_2), and in $C_3H_8 - O_2 - N_2$ with and without NO_2 as a chemical additive. The goal was to establish whether C_2H_2 or NO_2 could significantly affect the detonation sensitivity of hydrocarbon fuels.

2.2 Evaluating Mixture Sensitivity

In a smooth tube, the distance required for DDT is usually dominated by the early phases of laminar to turbulent transition of the flame. Since diffusion rates dominate during these phases, they will be mostly unaffected by chemical sensitization, characterized by the much faster rates of chemical kinetics. Not until the rate of turbulent mixing becomes similar to these chemical kinetic rates do we expect to see differences in propagation between sensitized and unsensitized mixtures. By using obstacles, we can cause a much more rapid transition to the high-speed turbulent deflagration regime as outlined in the previous section. In this regime, auto-ignition via the mixing of reactants and products plays a dominant role in the flame propagation; thus, we may expect that the effects of sensitization will be more prominent. It is also known that the run-up distance in a smooth tube is quite stochastic in nature, due to the extreme sensitivity of laminar to turbulent transition on the boundary conditions (wall roughness, ignition source, etc.). The run-up distance in a rough tube is, in general, much more reproducible and thus can provide a more accurate measure of the effectiveness of the sensitization process.

2.3 Experimental Apparatus

The experimental setup consisted of a 4.70 m steel detonation tube with a 0.145 m internal diameter. A schematic of the setup is presented in Fig. 2.1. The tube was lined with obstacles for reasons outlined previously. The obstacles used were steel orifice plates, spaced one tube diameter (0.145 m) apart. The plates were mounted on four steel rods to maintain the correct spacing. One of the obstacle sections is shown in the photograph of the apparatus in Fig. 2.2. The plates had an outside diameter of 0.145 m to match the tube inner diameter, and an orifice diameter of 0.109 m, giving a blockage ratio of 0.43. The blockage ratio is defined as:

$$\mathrm{BR} = 1 - \left(\frac{d}{D}\right)^2 \qquad (2.1)$$

Where d is the orifice diameter and D is the tube inner diameter. Previous work (Peraldi et al. [46]) has indicated that optimum flame acceleration can be achieved near this value of the blockage ratio. The last portion of obstacles could be removed to yield a section of smooth tube for making cell size measurements using smoked foils. In this setup, a 2.2 m section of obstacles were used to achieve DDT in the mixture tested, while the remaining

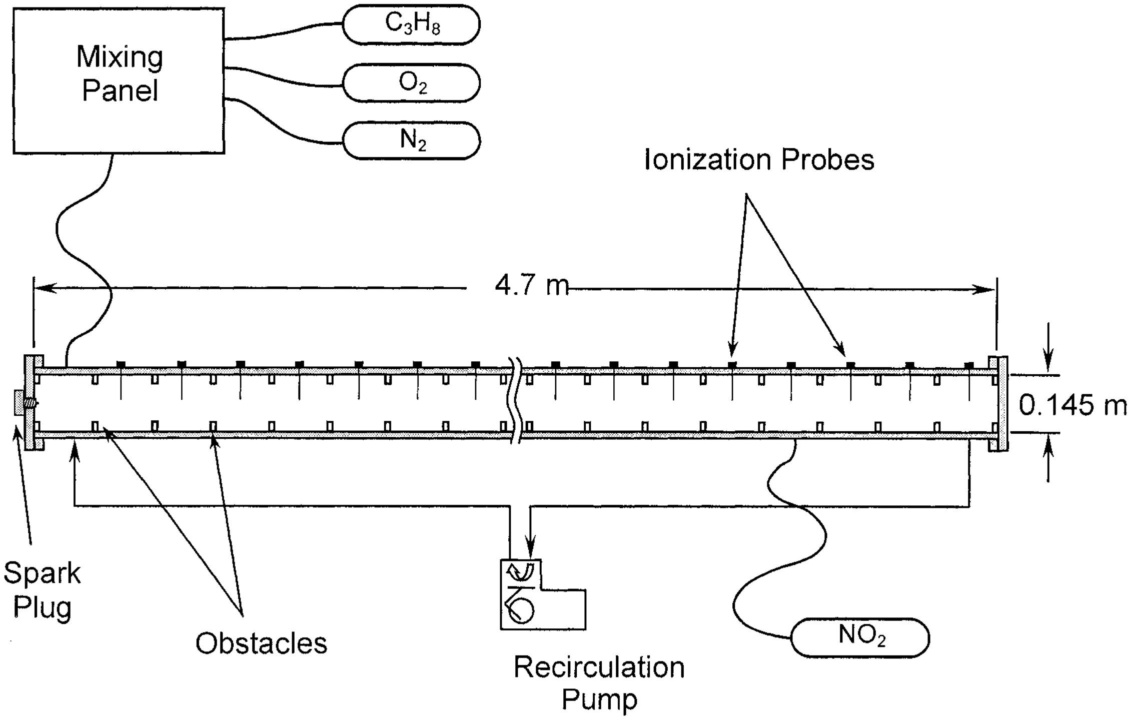


Fig. 2.1 Schematic of experimental apparatus

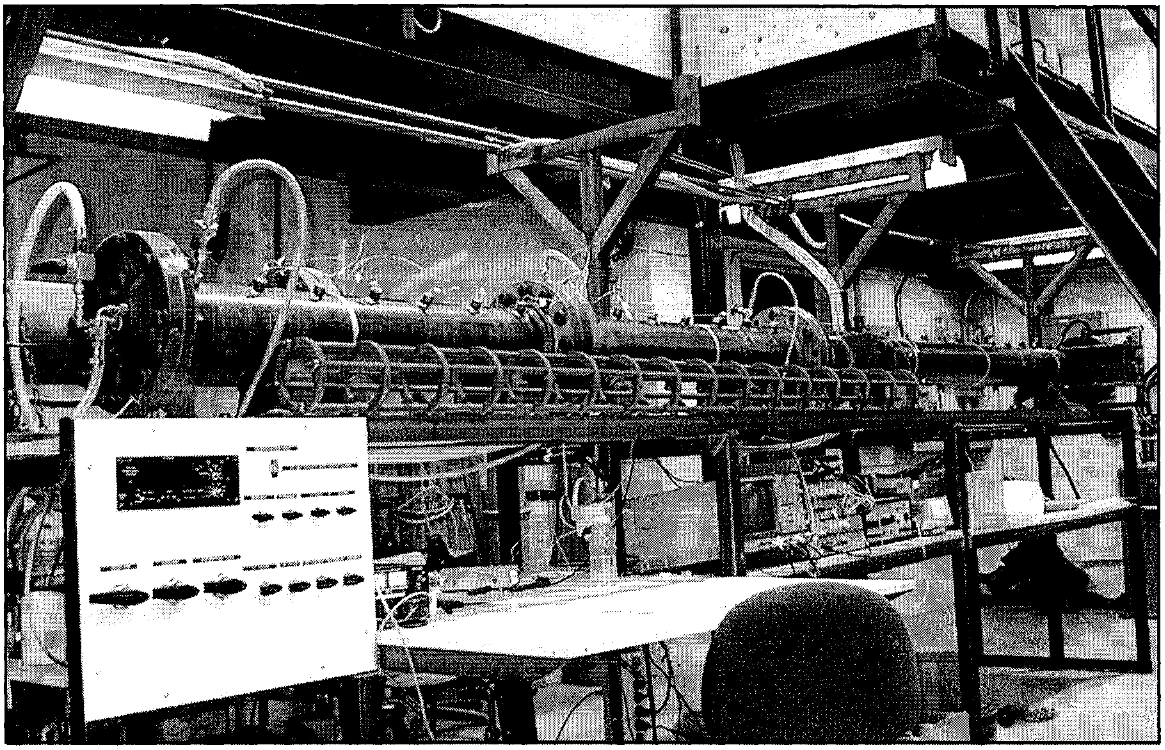


Fig. 2.2 Photograph of experimental apparatus

2.5 m were left free of obstacles to allow the characteristic transverse wave structure of the detonation to form. Experiments were conducted in both configurations with the same gas mixtures to confirm that the run-up distance was unaffected as long as DDT occurred within the first 2.2 m. Furthermore, the cell size measurements were compared with previous measurements from the literature and these were shown to agree (see Chapter 3). This indicates that the specific means used to initiate the detonation did not affect the fundamental cell size. Both circumferential soot-coated steel foils placed around the inner wall of the tube, as well as soot-coated Plexiglas plates placed diametrically across the inner diameter of the tube were used to record the cellular detonation pattern. The resulting cellular pattern was scanned, and the average cell width determined by taking an average over approximately 10 cell widths measured by hand. A photograph of the tube with the last obstacle section removed is shown in Fig. 2.2.

2.4 Mixture Selection and Preparation

The run-up distance was measured in mixtures of $C_3H_8/C_2H_2 - O_2 - N_2$ with varying proportions of propane and acetylene and in mixtures of $C_3H_8 - O_2 - N_2$ with and without nitrogen dioxide. Propane was chosen as the fuel due to its similarity with JP-10: Akbar et al. [19] measured the cell size of JP-10 – air mixtures and found that it matches that of C_3H_8 – air very closely. Furthermore, unlike JP-10, propane is in vapour form at standard temperature and pressure, making it much easier to control the mixture composition. Acetylene was used to evaluate the effectiveness of blending fuels because it is the most sensitive hydrocarbon fuel. NO_2 was chosen as the candidate sensitizer for reasons outlined in Chapter 1.

In a typical experiment, the tube was first evacuated to less than 200 Pa, and the required gases were then injected through a mixing panel to their required partial pressure. The bottled gases used were of at least 99.5% purity. The NO_2 was always injected directly into the tube in order to protect the mixing panel from corrosion. The final pressure for all experiments was always 1 bar. Once the gases were injected, a bellows type recirculation pump (Senior Flexonics Metal Bellows Division model MB-302) was used to thoroughly mix the gases. The mixtures were recirculated for a minimum of 15 minutes, displacing over 15 tube volumes. This provided excellent consistency in ignition and reproducibility in run-up distance (details are provided in Chapter 3). An automotive spark plug was used to ignite the mixture, driven through a standard fly-back circuit.

2.4.1 Acetylene Addition

All mixtures tested were stoichiometric, and are represented by the following formula:

$$\begin{aligned}(1-\alpha)C_3H_8 + \alpha C_2H_2 + 5(1-\alpha/2)(O_2 + \beta N_2) \\ \rightarrow (4-3\alpha)H_2O + (3-\alpha)CO_2 + 5(1-\alpha/2)\beta N_2\end{aligned} \tag{2.2}$$

Where α represents the molar fraction of C_2H_2 in the fuel, and β represents the nitrogen dilution. The value of β was fixed at 2.8 and 3.0, and in each case α was varied from 0 to 1 in order to evaluate the effects on run-up distance with respect to limit values corresponding to pure C_3H_8 fuel and pure C_2H_2 fuel.

2.4.2 NO_2 Addition

Great care was required in selecting a method to compare mixtures with and without NO_2 in order for the comparison to be meaningful. Indeed, since NO_2 is an oxidizer, if it is simply added to an existing mixture, it effectively changes the stoichiometry, thereby changing the sensitivity. The result being that NO_2 added to a stoichiometric or lean mixture could simply act as a diluent, while it could cause a rich mixture to approach stoichiometry. Such energetic changes will affect the run-up distance. We sought to evaluate the effect of NO_2 resulting exclusively from kinetic changes in the chemical reactions. A rigorous method for comparing mixtures with and without NO_2, which eliminated energetic differences, was therefore required.

Regardless of whether a mixture contains NO_2, it is composed of three ingredients: propane as the fuel, oxygen as the oxidizer, and nitrogen as a diluent. The ratio of atomic oxygen to propane determines the stoichiometry, and the ratio of nitrogen to oxygen is the nitrogen dilution. When evaluating these ratios, 1 mole of NO_2 was therefore considered equivalent to 0.5 mole of N_2 and 1 mole of O_2. To eliminate energetic differences, the following two criteria are proposed. First, all the mixtures should be stoichiometric, so the equivalence ratio is always 1, or equivalently, there are always 10 oxygen atoms to one propane molecule, regardless of the source of oxygen (O_2 or NO_2). Second, it is proposed to compare mixtures with identical nitrogen dilution (i.e. the ratio of atomic nitrogen to atomic oxygen), again regardless of the source of oxygen and nitrogen (O_2, N_2 or NO_2).

Practically, this was done as follows. The unsensitized mixture (Eq. 2.3) was prepared by selecting a nitrogen dilution, labelled β. The equivalent sensitized mixture (Eq. 2.4) was then prepared by first selecting the amount of NO_2 desired. This fixes parameter c. The amount of O_2 and N_2 (parameters a and b) were then adjusted to achieve the same dilution as in Eq. 2.3. The required relations for a and b are given in Eq. 2.5.

$$\mathrm{C_3H_8} + 5(1\mathrm{O_2} + \beta \mathrm{N_2}) \rightarrow 4\mathrm{H_2O} + 3\mathrm{CO_2} + 5\beta(\mathrm{N_2}) \tag{2.3}$$

$$\mathrm{C_3H_8} + 5(a\mathrm{O_2} + b\mathrm{N_2} + c\mathrm{NO_2}) \rightarrow 4\mathrm{H_2O} + 3\mathrm{CO_2} + 5\beta(\mathrm{N_2}) \tag{2.4}$$

$$a = 1 - c$$
$$b = \beta - \frac{c}{2} \qquad (2.5)$$

The amount of NO_2 was varied from a 0.1 to a 0.5 molar ratio of NO_2 to fuel concentration. This can be expressed also based on the ratio of partial pressures:

$$0.1 \leq \frac{P_{\mathrm{NO_2}}}{P_{\mathrm{C_3H_8}}} \leq 0.5 \qquad (2.6)$$

The nitrogen dilution was varied from 0 to 3.76, the latter corresponding to the N_2 to O_2 ratio of air. In order to confirm that these two mixtures (Eqs. 2.3 & 2.4) have the same energetics, the CJ temperature was calculated using the NASA Chemical Equilibrium with Applications (CEA) code [47] for both mixtures over the range of nitrogen dilution tested and for the maximum addition of NO_2. The results are presented in Fig. 2.3. From this graph, we clearly see that the CJ temperature for mixtures sensitized with NO_2 is

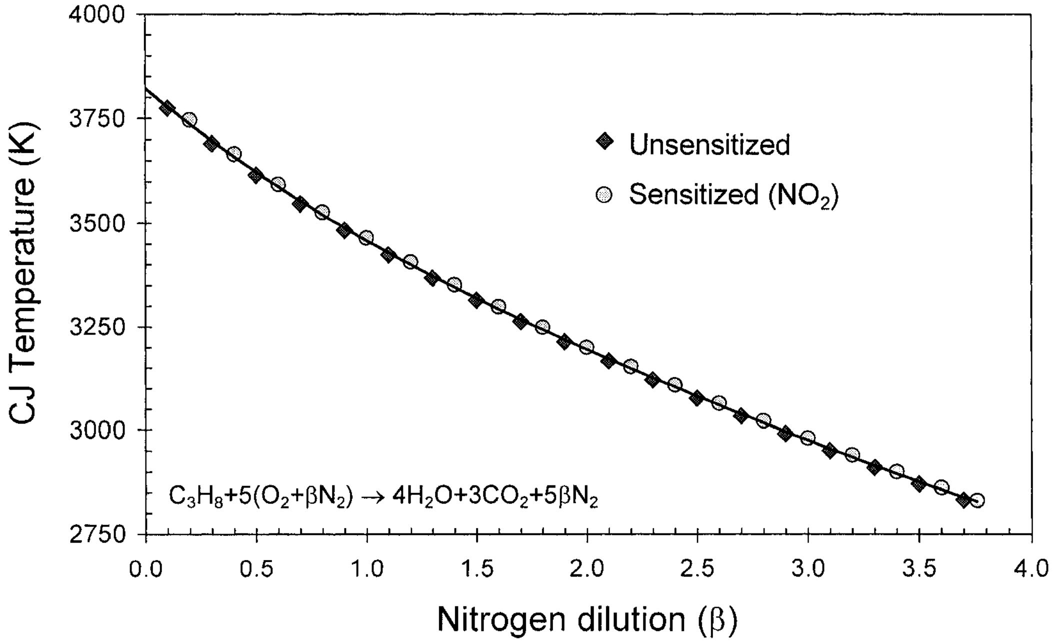


Fig. 2.3 Effect of NO_2 on the CJ temperature

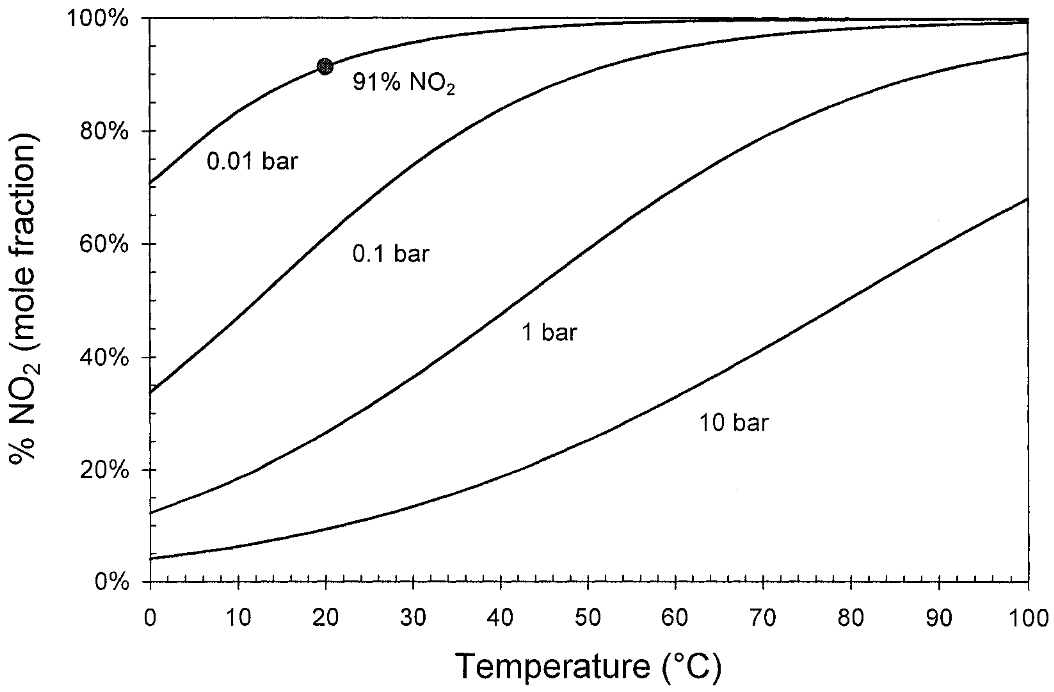


Fig. 2.4 Composition of NO_2/N_2O_4 as a function of temperature and pressure

essentially the same as that of the mixtures without NO_2. The fact that all the points lie on the same curve indicates that the energy release is the same for a given nitrogen dilution. In other words, the method of mixture comparison outlined above effectively eliminates the potential energetic effect of NO_2, and has allowed us to precisely evaluate its sensitizing effect on DDT in $C_3H_8 - O_2 - N_2 - NO_2$ mixtures.

Gaseous nitrogen dioxide is actually an equilibrium composition of NO_2 and N_2O_4. The equilibrium concentration is a function of temperature and the partial pressure of NO_2/N_2O_4. The equilibrium fraction of NO_2 was calculated using CEA [47] for a range of temperatures and pressures, and the results are shown in Fig. 2.4. As the amount of NO_2/N_2O_4 gas used was always of the order of 0.01 bar partial pressure and experiments were conducted at room temperature (approximately 21°C), it was always assumed that the gas composition was 90% NO_2 and 10% N_2O_4 (mole fraction) when evaluating the stoichiometry and nitrogen dilution. Therefore, Eq. 2.4 becomes:

$$C_3H_8 + 5[aO_2 + bN_2 + c'(0.9NO_2 + 0.1N_2O_4)] \rightarrow 4H_2O + 3CO_2 + 5\beta(N_2) \tag{2.7}$$

$$c' = \frac{c}{1.1} \tag{2.8}$$

Now, c is the amount of NO_2 desired, as stated in Eq. 2.4, and c' corresponds to the actual amount of gas injected with respect to the other constituents. In the following sections, when referring to NO_2, it is understood that the equilibrium composition of NO_2/N_2O_4 described above actually exists.

2.4.3 Mixture Preparation with NO_2

After evacuation of the tube, a small amount of N_2 was first injected as a buffer for the panel. This was accounted for as part of the overall mixture. The NO_2 was then injected directly into the tube. Under vacuum, the tube leak rate was measured as 0.01 kPa/min, determined by evacuating the tube, then sealing all valves and monitoring the pressure rise in about one hour. However, after injection of the NO_2, the pressure reading would stabilize, or even decrease, indicating a non-equilibrium in the gas composition (NO_2 vs. N_2O_4) just after injection. This effect was not present with the other gases used, which do not have an equilibrium state composed of two different molecules. In order to determine the actual amount of NO_2 present, it was therefore necessary to wait until the nominal leak rate was re-established. The amount of NO_2 added was then calculated as:

$$P_{NO_2} = P_2 - P_1 - (r_{\text{leak}} \times t_{\text{inj}}) \tag{2.9}$$

Where P_2 and P_1 are the final and initial pressure readings, r_{leak} is the leak rate, and t_{inj} is the time from the end of injection to the re-establishment of the nominal leak rate. In other words, it is assumed that the tube has the same leak rate, and the amount leaked in must be compensated for. The gas that leaks in is air from the room. The amount leaked in was generally less than 0.3 kPa (30 min fill time), while the amount of O_2 and N_2 in the final mixture is two orders of magnitude more. Furthermore, since air is primarily composed of N_2, the amount leaked can be safely assumed to be composed of N_2 in evaluating the final mixture composition. The rest of the gases are then injected sequentially to the required partial pressure. The rest of the gas preparation was described at the beginning of section 2.4.

2.5 Diagnostics

2.5.1 Time-of-Arrival Measurement

Ionization probes, spaced 1 tube diameter apart, were located along the length of the tube to monitor the time-of-arrival of the combustion wave. The circuit used to power the ionization probes is described in detail in Appendix A. The probes are composed of two electrodes (Fig. 2.5) charged by a capacitor to 200-400 V. Upon passage of the combustion wave, the large ion concentration causes a short between the electrodes. A voltage is then immediately established across a resistor in series with the probe and capacitor. The resistor voltage is monitored via a digital Lecroy oscilloscope, and the resulting signal provides the time-of-arrival (TOA) of the combustion wave at the probe location. The distance between adjacent probes is then divided by the time between successive TOA signals, giving an average velocity between probes. For simplicity in presenting the results, this velocity is taken as occurring at the midpoint between successive probes. This results in a plot of combustion wave velocity against the distance measured along the tube. The run-up distance is the distance from the point of ignition to the location where the combustion wave first achieves the detonation velocity. The error in evaluating the run-up distance can be evaluated as ± 1/2 of the distance between the probes. This error is based on the assumption that if the average velocity between two probes is at or above the detonation velocity, then the transition to detonation occurred somewhere between these probes. However, the exact location cannot be determined more precisely. For this reason, the run-up distance is reported as the midpoint between these probes.

2.5.2 Long vs. Short Ion Probes

Initial experiments were carried out using short ion probes. The short probes were advantageous in that they did not penetrate significantly into the flow, and were therefore not prone to being damaged. However, a concern arose that the orifice plate obstacles were shielding the short ion probes from the combustion front, as illustrated in Fig. 2.5. This would lead to late TOA signals that would not reflect the true propagation speed of the combustion wave. In order to evaluate this effect, long ion probes were built, using a stronger coaxial design. A stainless steel tube was used as one electrode, while an insulated needle inserted through the tube served as the other electrode. This design allowed the ion probe to penetrate all the way to the centreline of the detonation tube.

The relative performance of these two designs was evaluated in the first portion of the tube, equipped with six diametrically opposed ports. Mixtures up to $\beta = 2.0$ could be detonated in this configuration. Fig. 2.6 shows raw output from both short and long ion probes opposed in the first six ports of the tube for the same experiment with a $\beta = 2.0$ mixture. The ports are equally spaced 150 mm apart. The output from the probes is a sharp negative-going signal when the flame passes across the electrodes. The magnitude of the signal reflects the ion density in the flame zone. Time zero is taken from an output of the ignition circuit and corresponds to the spark discharge. Both outputs presented are plotted on the same time scale, and the signals labelled 1 through 6 correspond to opposing probes.

The long ion probes clearly reflect the acceleration of the combustion wave, all the way to the onset of detonation between locations 5 and 6. The section labelled "extra probes" corresponds to the continuation of the tube, which was not equipped with opposing ports for short probes. On the other hand, the short probes do not give a good picture of the flame acceleration process. The first short probe does not see the combustion front until after the *second* long probe has signalled its passage. This is due to the orifice plate configuration, which results in a series of interconnected combustion chambers along the length of the tube. This leads to a tendency for the flame to jet through successive orifices along the centreline of the tube, and only later reach the sides. The short probes are thus shielded from the passage of the flame. Furthermore, the short probes can give inconsistent velocities, as illustrated by the shorter delay between signals 2 – 3 than between 3 – 4. Nevertheless, the error in establishing the location of onset of detonation was never more than +1 port with the short probes relative to the location given by the long ion probes. In the example shown, both sets of probes indicate the same location, between ports 5 and 6.

In light of these results, the short ion probes were replaced by long ion probes, but the results obtained with short probes were kept with the knowledge that they may lead to a slight over-prediction of the run-up distance.

2.5.3 Soot Foils

For a number of experiments, the characteristic detonation cell width (λ) was determined by the method of soot foils. For this technique, an oil lamp was used to coat a thin steel foil or a Plexiglas plate with a thin layer of soot. The foils were then placed circumferentially around the inside of the tube, while the plates were placed diametrically across the inside of the tube. Both were placed at the end of a 2.5 m smooth section of the tube. After an experiment, the foil and/or plate were removed. In the case of the foils, a picture was taken, and then loaded onto a PC though an optical scanner, while the plates were scanned directly. The scanned image was then used to measure the cell width across approximately 10 cells. The cell width reported is the average cell width measured, and the error given as the difference between the largest and smallest cell measured. Fig. 2.7 shows a typical scan of a sooted Plexiglas plate, as well as an interpretive representation of the cellular pattern. The detonation travelled across the plate in the direction of the arrow. Parallel lines are traced along the edges of adjacent cells so that the horizontal spacing between these lines gives the cell width.

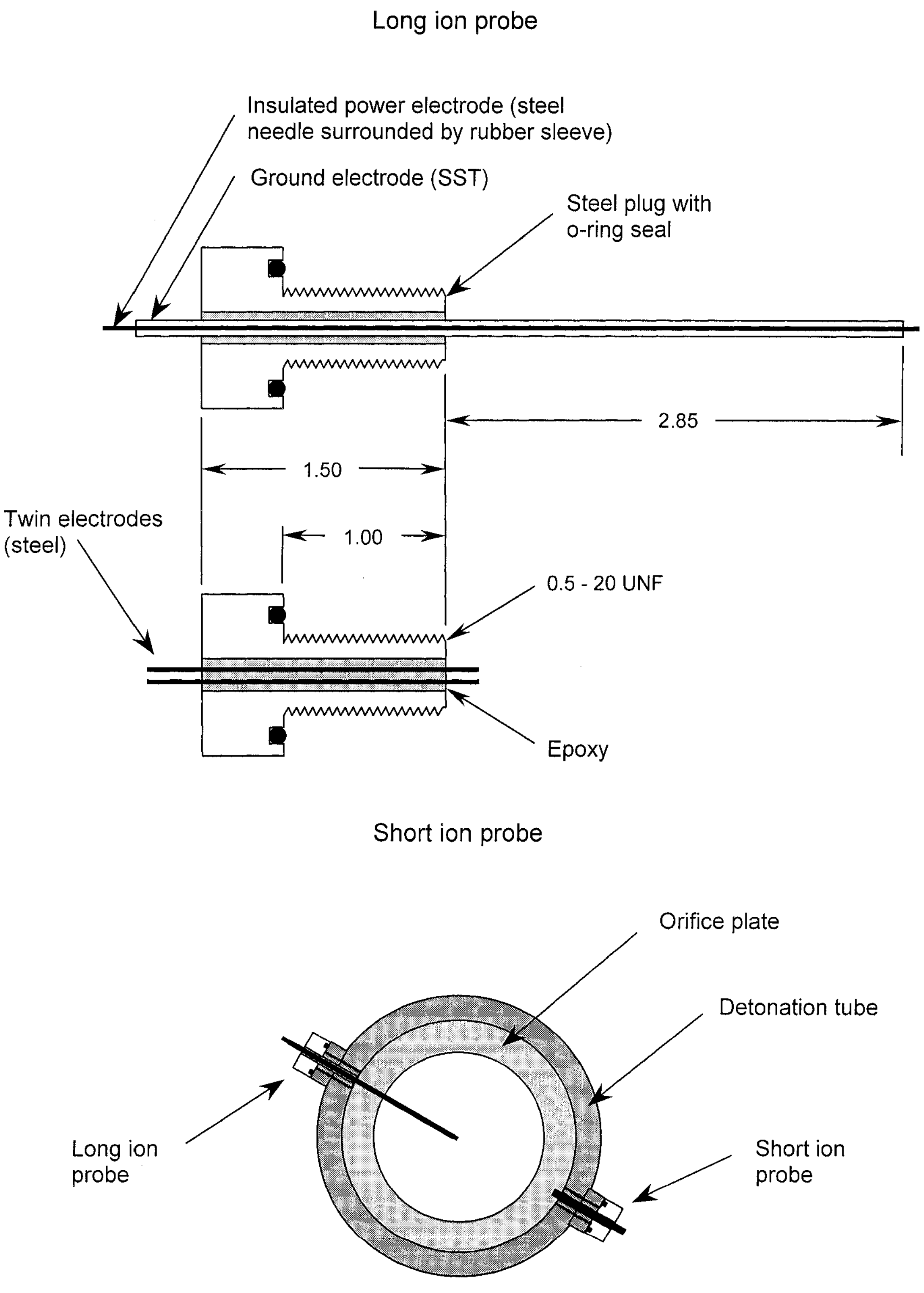


Fig. 2.5 Schematic of long and short ion probes with cross-sectional view of tube installation

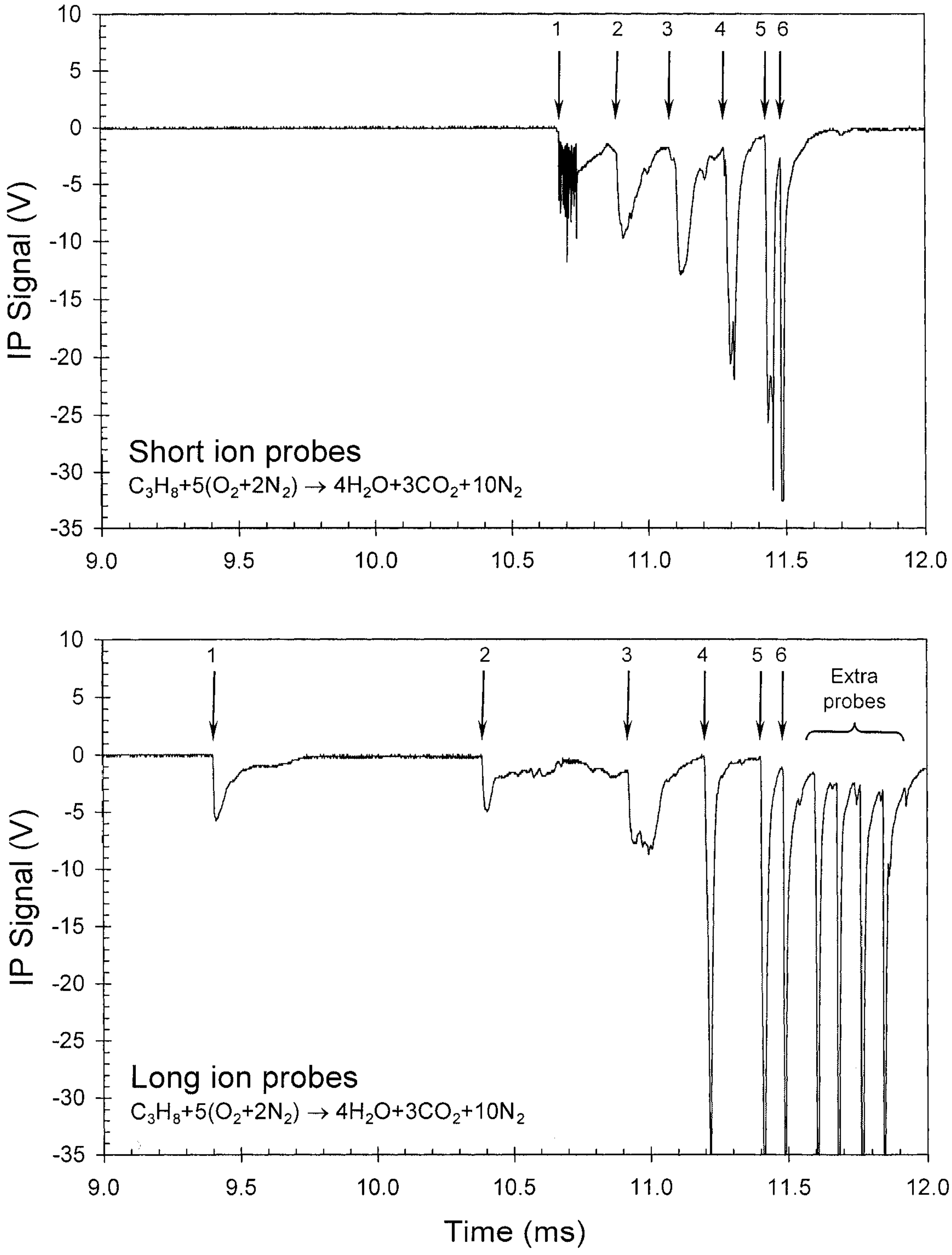


Fig. 2.6 Comparison of raw output for short and long ion probes for the same experiment with opposing probes numbered 1 – 6.

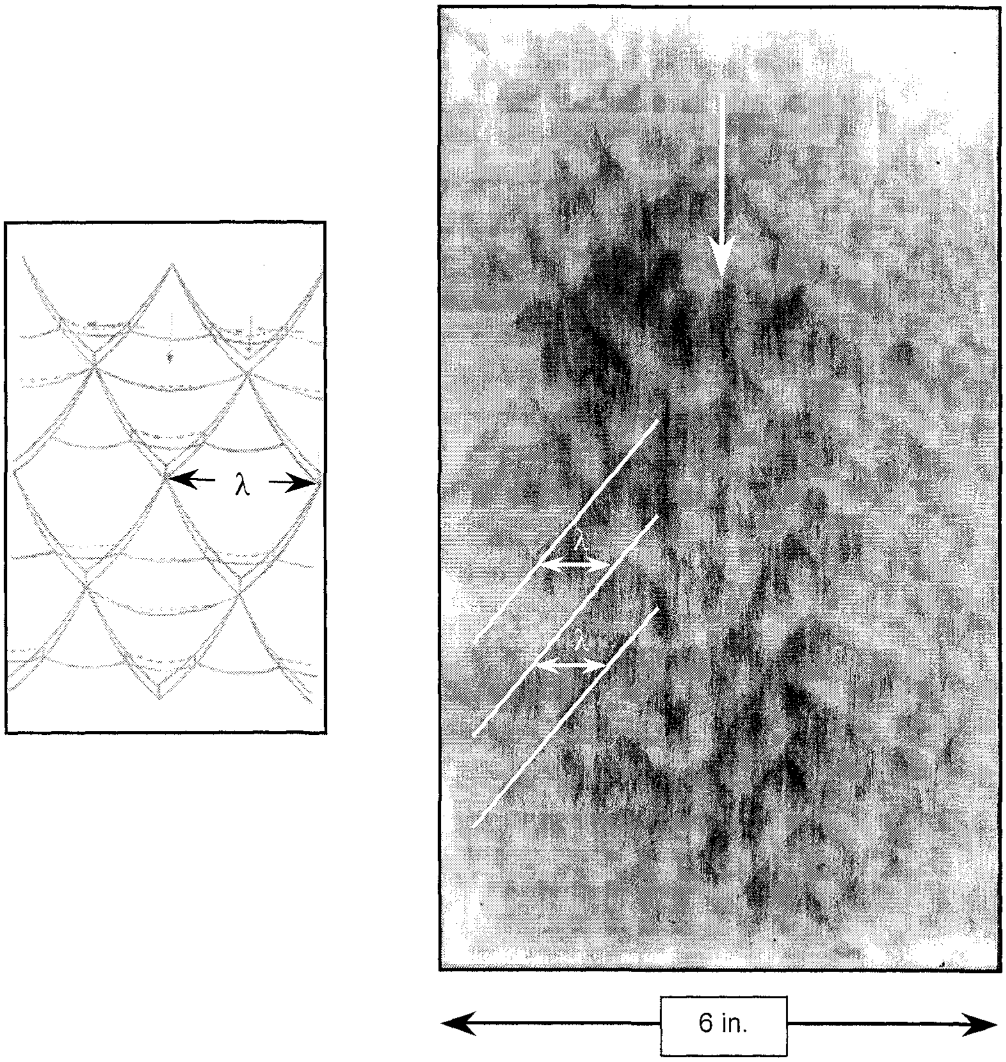


Fig. 2.7 Left: Theoretical representation of shock interactions leading to cellular pattern. Right: Smoke foil record of C_3H_8 - O_2 - N_2 experiment at $\beta = 2.4$ (50 % of full scale). Vertical arrow indicates direction of propagation.

Chapter 3 Results and Discussion

3.1 Overview

Experiments were performed for mixtures of $C_3H_8 - O_2 - N_2$ over a range of nitrogen dilution (β) from 0.0 (i.e. no nitrogen dilution) to 3.76 (nitrogen to oxygen ratio in standard air). The results established a baseline for run-up distance as a function of nitrogen dilution, and cell width as a function of nitrogen dilution. The following experiments were aimed at investigating the effect of acetylene and nitrate addition. This was achieved by measuring run-up distance and cell width over the same range of nitrogen dilution with varying concentrations of the additives.

3.2 Run-up Distance Without Chemical Additives

Experiments were performed initially for the stoichiometric mixtures:

$$C_3H_8 + 5(O_2 + \beta N_2) \rightarrow 4H_2O + 3CO_2 + 5\beta(N_2) \qquad (3.1)$$

The run-up distance to detonation was measured by generating the velocity profile of the combustion wave as it travelled down the tube. Results for a value of $\beta = 3.1$ are presented in Fig. 3.1. The plot shows the velocity of the combustion wave vs. the distance along the tube for two experiments. The reproducibility of the results is clearly illustrated in this example. Each data point corresponds to the average velocity between adjacent probes. The upper dashed line indicates the theoretical Chapman-Jouguet detonation velocity for this mixture, which was calculated using the NASA Chemical Equilibrium with Applications (CEA) code [47]. The lower dashed line indicates the experimental detonation velocity observed. It is simply the average velocity after the wave reaches steady state. The deficit from the theoretical CJ velocity is attributable to the presence of obstacles. This effect has been observed and described by numerous researchers. In fact, studies of detonation propagation in very rough tubes by Guenoche and Manson [48],

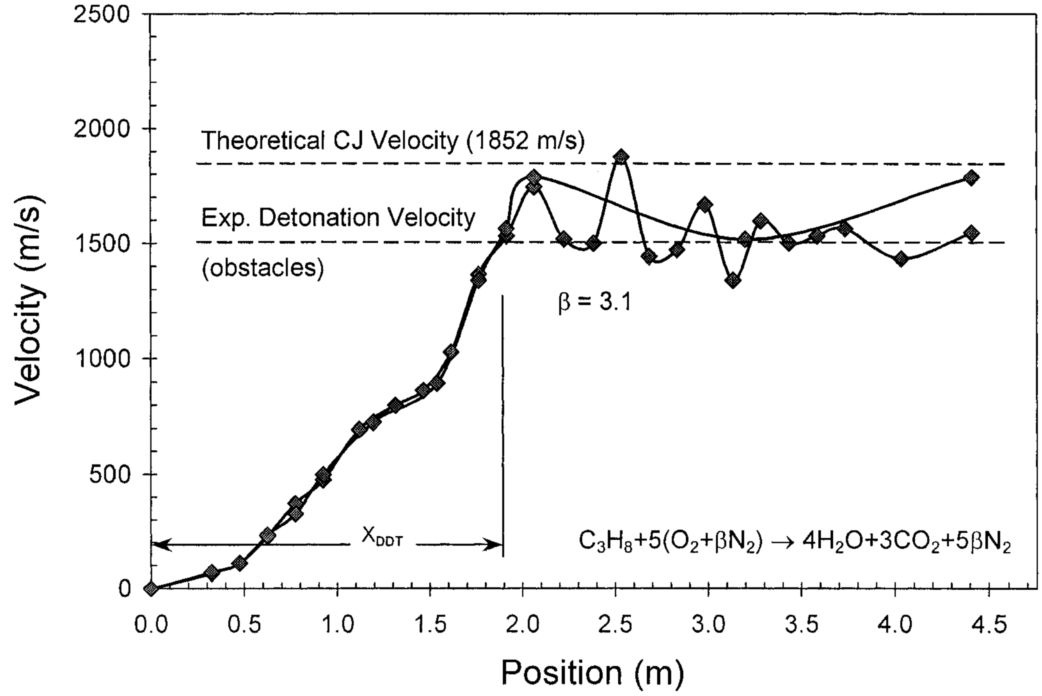


Fig. 3.1 Typical velocity profiles for $C_3H_8 - O_2 - N_2$

Brochet and Manson [49], and Zel'dovitch *et al.* [50] have identified detonation velocities less than 50% of the theoretical C-J value.

The significant oscillations observed after the onset of detonation are also caused by the obstacles. They modify the ideal propagation mechanism by giving rise to complicated shock interactions. Therefore, there is no longer a clear demarcation between the leading shock and the combustion front. Due to the altered propagation mechanism, the term *quasi-detonation* is often used to refer to these waves. However, in cases where a portion of obstacles was removed to make cell size measurements, the wave was observed to quickly transition to the CJ velocity, and the oscillations disappeared. Indeed, Lee *et al.* [51] and Knystautas *et al.* [52] have shown that a quasi-detonation emerging from a rough tube section into a smooth tube will immediately jump to the theoretical C-J detonation velocity provided the transition is not accompanied by an area change that is too large.

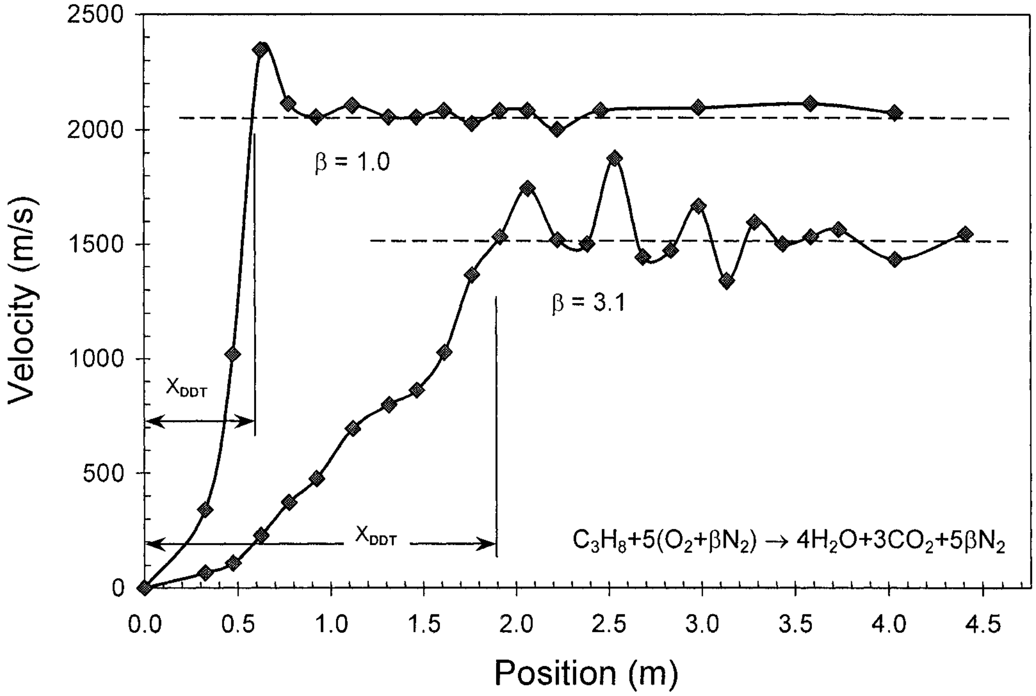


Fig. 3.2 Effect of nitrogen dilution on the velocity profile

The run-up distance, labelled X_{DDT}, is the distance from the igniter to the location where the wave first reaches the detonation velocity. Since the instrumentation was limited to one ion probe per tube diameter (lengthwise), the location is more simply taken as the mid-point between adjacent probes where the detonation velocity is first achieved, as described in Chapter 2.

Fig. 3.1 indicates that the combustion wave quickly accelerates to a high-speed (supersonic) turbulent deflagration. Clearly, the later stages of acceleration described in Chapter 1 (intense turbulence and shock induced mixing) are present for the majority of the run-up distance. The pressure disturbances sent ahead of the combustion wave compress and heat the unburnt gases until shock-induced ignition leads to the onset of detonation, accompanied by a characteristic overshoot in velocity. In this case the run-up distance is ~ 1.9 m. Despite the complex nature of DDT, the results were very reproducible for a given mixture. The largest fluctuations in run-up distance observed were ±1 tube diameter.

The effect of reducing nitrogen dilution is to reduce the run-up distance, as can be seen in Fig. 3.2. This figure shows the same velocity profile described above along with a sample velocity profile for approximately 1/3 the nitrogen dilution, indicated by $\beta = 1.0$. The low dilution mixture accelerates much more rapidly and detonates within ~ 0.6 m. This is mostly due to the increased heat release of the combustion as the mixture becomes less dilute. Each stage of the flame acceleration described earlier is enhanced by the increase in temperature. It is well known that the laminar flame speed is higher in less dilute mixtures [53]. The expansion of the products is greater, leading to earlier onset of turbulence, and a stronger feedback loop, as described in Chapter 1. Ultimately, the critical conditions for detonation are reached much earlier.

The reduced intensity of the oscillations after onset of detonation is attributable to the increased sensitivity of the mixture. The cell size for the $\beta = 1.0$ mixture is 5-6 mm, versus 36 mm for the $\beta = 3.1$ mixture. Thus, almost 7 times as many cells fit across the

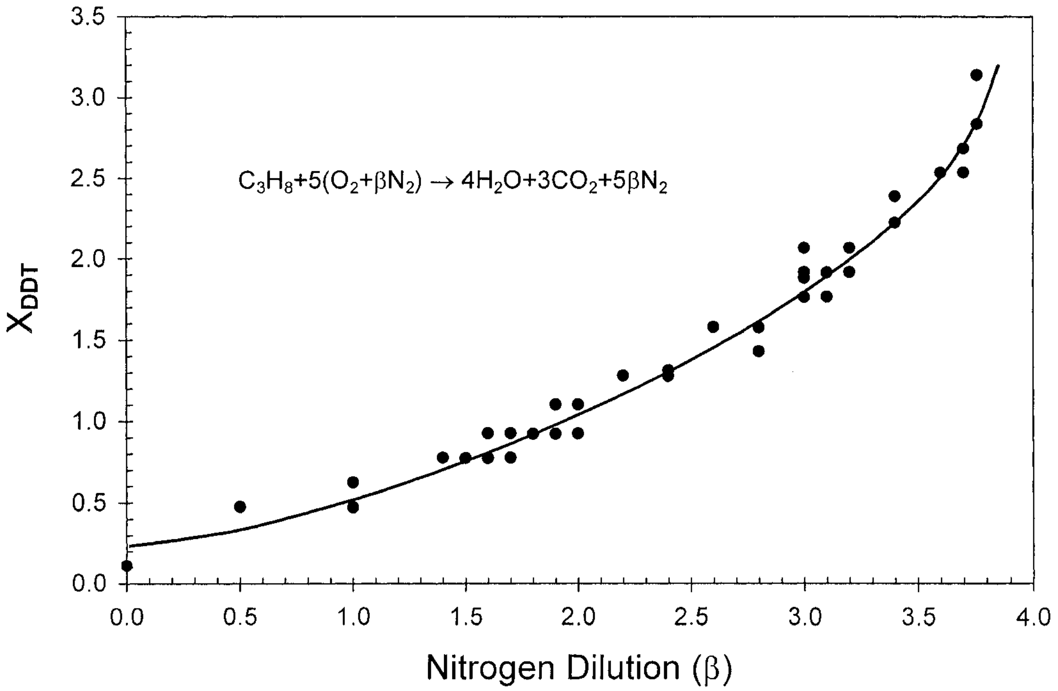


Fig. 3.3 Run-up distance against nitrogen dilution for mixtures without additives

obstacle rings in the more sensitive mixture. The characteristic length scale being much shorter, the low-β mixture is less sensitive to boundary effects, and this results in smaller fluctuations. For this experiment, the obstacles had been removed in the latter portion of the tube (from 2.2 m to the end) in order to measure cell size. The detonation is therefore seen to accelerate up to the CJ velocity, and the fluctuations are reduced.

A summary plot of the results for run-up distance in stoichiometric $C_3H_8 - O_2 - N_2$ mixtures for varying nitrogen dilution is shown in Fig. 3.3. The plot represents the run-up distance vs. the nitrogen dilution (β) for over 80 shots (repeated results are overlaid). A trend line has been added through the data points. The tight grouping of the data around the trend line confirms the reproducibility of the results. As expected, the run-up distance increases as the nitrogen dilution is increased, ranging from 0.1 m for propane-oxygen to 3 m for propane-air. This data served as a baseline for the experiments with chemical additives.

3.3 Run-up Distance with Acetylene

Fig. 3.4 shows a sample of velocity profiles for each of the α values tested for $\beta = 2.8$. The dashed line represents the average detonation velocity. The significant oscillations in the early stages of flame acceleration are attributed to the use of short ion probes for these experiments. The result presented for $\alpha = 0.0$ corresponds to a test conducted with long ion probes. It matched short probe results (not shown) and thus confirms the observation made in Chapter 2 that the determination of run-up distance is almost unchanged by the use of short probes. The tests for other values of α were therefore not repeated with long probes.

It is clear from this figure that the run-up distance reduces as the acetylene concentration is increased. The run-up distance is bound between ~ 1.5 m for pure propane and ~ 0.75 m for pure acetylene. The run-up distance as a function of α is plotted in Fig. 3.5 for all the experiments at $\beta = 2.8$. The data was collected at the values of α indicated in Fig. 3.4, and have been spread out for visual purposes only. From the trend line drawn through the points, it is obvious that the effect of acetylene addition is gradual. The experiments for $\beta = 3.0$ show the same result. Since there is no radical departure from

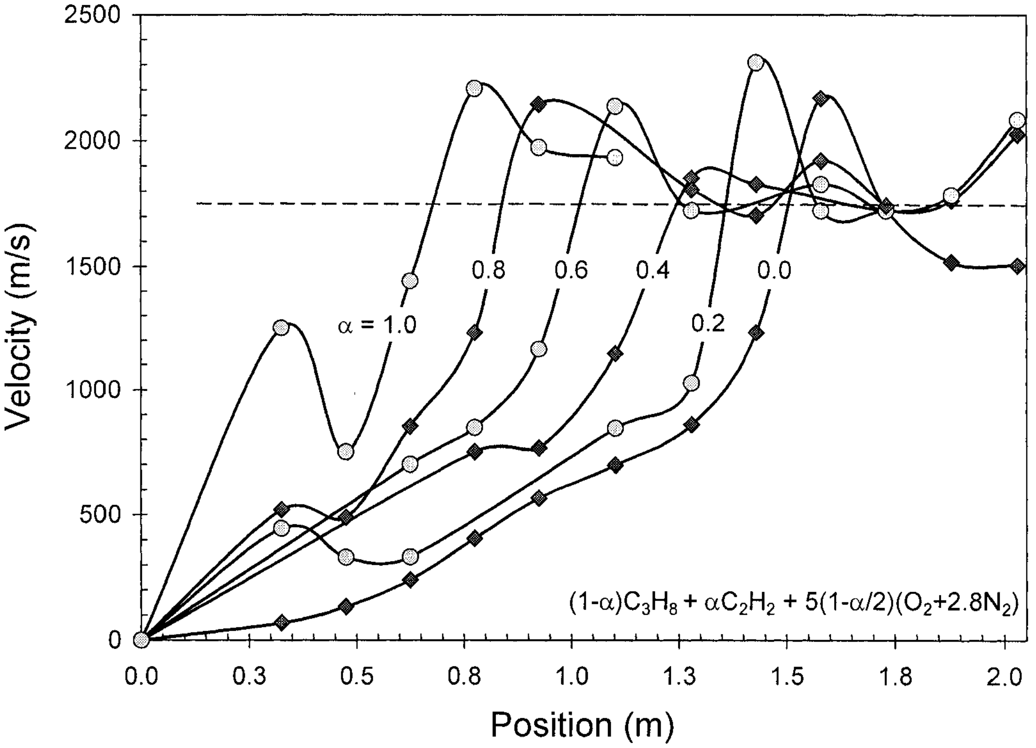


Fig. 3.4 Velocity profile variation with acetylene concentration

C_3H_8 sensitivity with a small amount (ideally, a few percent) of C_2H_2, it cannot be considered as an effective additive.

3.4 Run-up Distance with NO_2

Experiments were performed for the stoichiometric mixtures:

$$C_3H_8 + 5(aO_2 + bN_2 + cNO_2) \rightarrow 4H_2O + 3CO_2 + 5\beta(N_2) \tag{3.2}$$

The values of *a*, *b*, and *c* are selected as described in Chapter 2. Typical velocity profiles are presented in Fig. 3.6 for sensitized and unsensitized mixtures at two levels of nitrogen dilution, corresponding to $\beta = 1.0$ and $\beta = 3.1$. In both cases, the NO_2 addition is the maximum tested (NO_2-to-fuel ratio = 0.5, or equivalently, $c = 0.1$). In terms of using NO_2 as a fuel additive, this is a very significant amount, corresponding to a sensitized fuel containing 33% NO_2. The graph again shows the velocity of the combustion wave as it

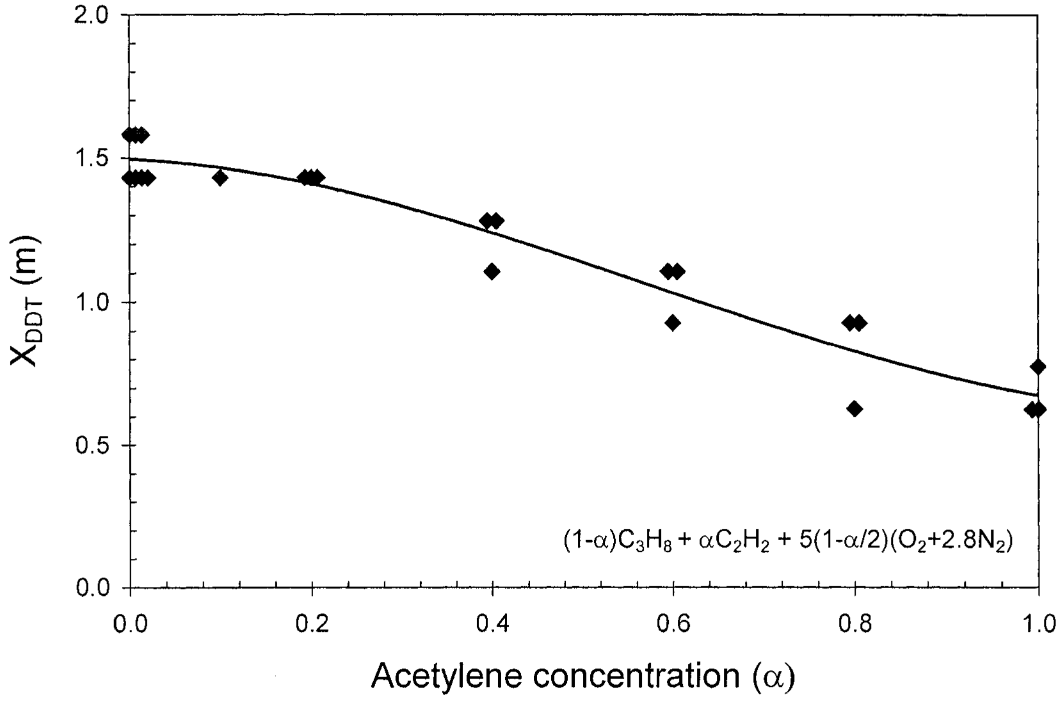


Fig. 3.5 Variation of run-up distance with acetylene concentration

accelerates down the tube from the point of ignition. For both values of β presented, it is clear that the run-up distance is unaffected by the NO_2 addition. The apparent variation for the high-β case corresponds to about 1 tube diameter and is within the scatter of the results.

A summary of all the run-up distance measurements taken with and without NO_2 is presented in Fig. 3.7. The graph shows X_{DDT} as the nitrogen dilution is increased for both unsensitized mixtures (the baseline data described above) and mixtures with increasing amounts of NO_2 (NO_2-to-fuel ratio = 0.1 to 0.5). If we focus on any given value of nitrogen dilution, we see that there is no change in run-up distance as NO_2 is added. This is true for the whole range tested: all the points lie along the same trend line. In none of the cases has NO_2 sensitized the mixture. This implies that NO_2 simply acts as an oxidizing agent, equivalent to the O_2 it replaces. In other words, its effect is purely energetic.

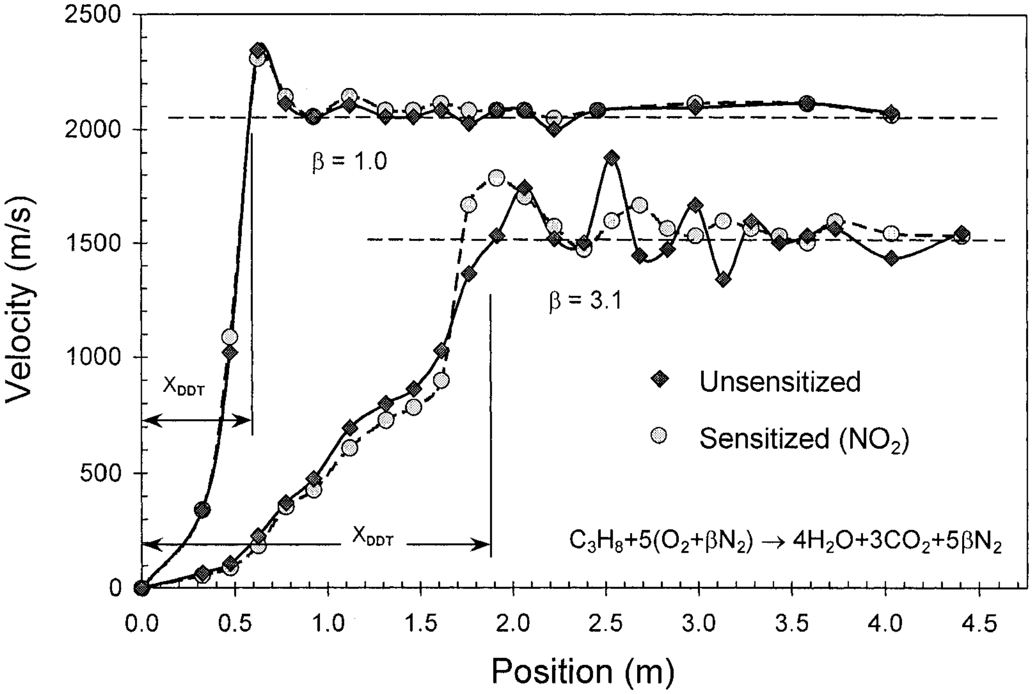


Fig. 3.6 Effect of NO_2 on the velocity profile

3.5 Effect on Cell Size

In order to confirm the run-up distance data collected, cell width measurements were taken for a number of the experiments described in the previous sections. Data were collected for $\beta = 1.0, 1.4, 2.4$, and 3.0 without NO_2, and with the NO_2-to-fuel ratio = 0.5 (i.e. the highest additive content tested). Fig. 3.8 shows cell width in millimetres as a function of percentage of nitrogen in the total mixture with pictures of two of the experimental results overlaid. The percentage of nitrogen was selected rather than the nitrogen dilution in order to improve the linear fit with respect to the logarithm of the cell width. They are related by:

$$\% N_2 = \frac{5\beta}{1+5(1+\beta)} \times 100 \qquad (3.3)$$

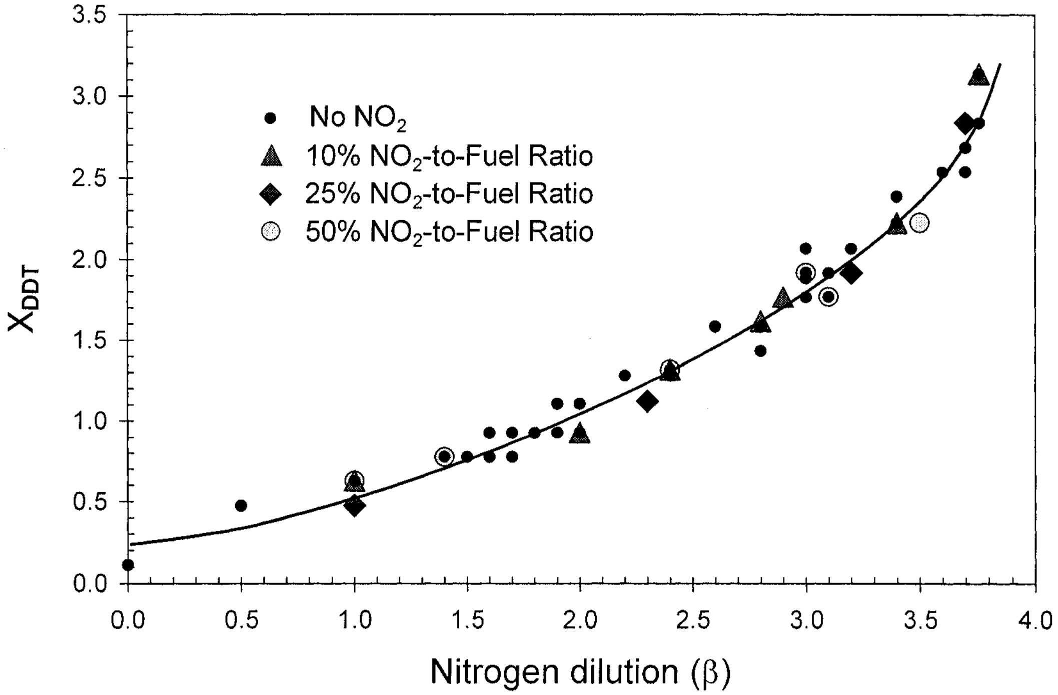


Fig. 3.7 Effect of NO_2 on run-up distance

The equations for determining the NO_2 mixtures with the same nitrogen dilution (therefore the same % N_2) as mixtures without NO_2 are described in Chapter 2. Data from Knystautas *et al.* [29] for C_3H_8 - O_2 - N_2 mixtures along with an exponential fit (straight line on logarithmic scale) are presented for reference. A number of experiments were done at each value of β, and the data has been spread out only to help in visualizing the data points and error bars. The cell width plotted for each experiment corresponds to an average from measurements across a number of cells. The error bars represent the spread between the largest and smallest cell measured.

Due to the irregularity of the cells, a large scatter is typical of cell width measurements. With this is mind, it is apparent that the measured cell widths correspond quite well with those of Knystautas *et al.* [29], especially at lower values of nitrogen dilution. As the nitrogen dilution increases, the cells become more irregular and fewer cells can "fit" across the tube, making the appropriate cell width more difficult to determine. It is

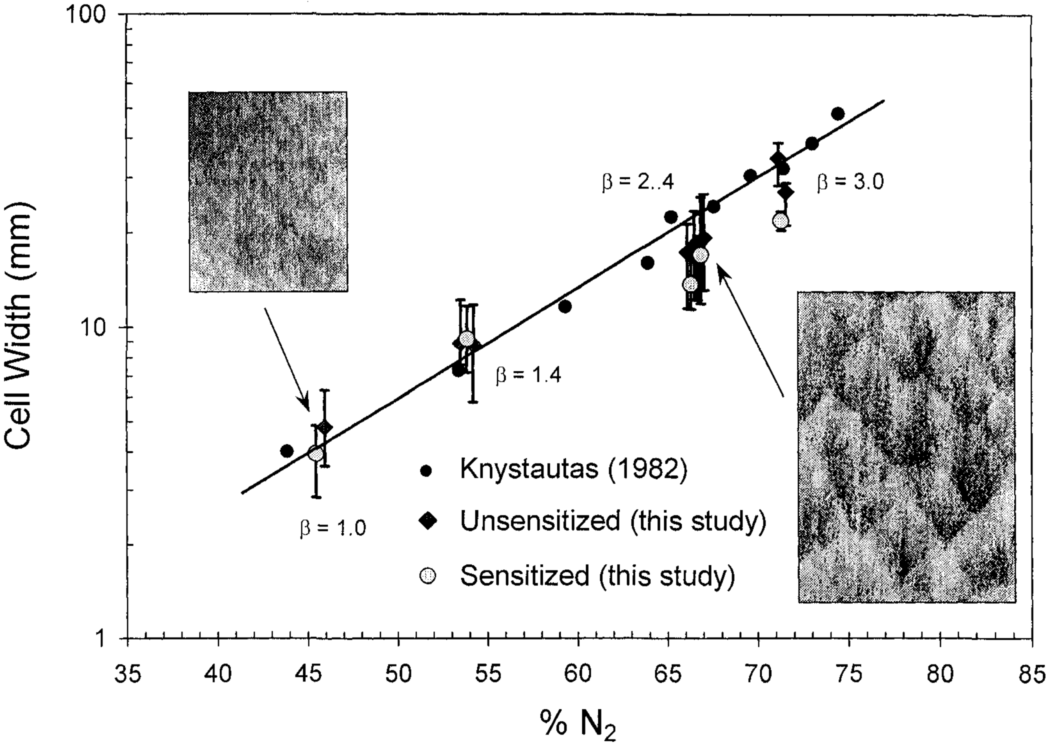


Fig. 3.8 Effect of NO_2 on cell width

particularly interesting to note that all the cell widths in mixtures with NO_2 addition fall within the error bars of the mixtures without additive. This confirms the conclusions of the previous section, i.e. that NO_2 has no sensitizing effect on these mixtures.

3.6 Discussion of Results

3.6.1 Acetylene results

The results for C_2H_2 addition indicate that the sensitivity of the fuel varies gradually as the proportion of additive is increased. In fact, the run-up distance of the fuel blend is almost a linear interpolation between that of each of its constituents. The work of Westbrook & Haselman [31] indicated that the presence of a small amount of ethane in methane had a significant effect on the ignition kinetics (e.g. 5 % ethane reduced the ignition delay by half). It was proposed that the presence of H atoms from the ethane decomposition accelerate the initiation of chain branching of the very stable CH_4 molecule. The results presented here indicate that the acetylene does not establish an analogous kinetic path to accelerate reactions. Since these results were obtained by using the most sensitive hydrocarbon fuel, this method for sensitization in fuels such as C_3H_8 and JP-10 can be effectively ruled out.

3.6.2 NO_2 results

The results presented also clearly indicate that NO_2 does not sensitize $C_3H_8 - O_2 - N_2$ mixtures for deflagration to detonation transition. This appears to be in contradiction with results indicating significant reductions in induction delay for both diesel fuels [33,34] and hydrocarbon fuels [35,36] with very small amounts of nitrate compounds or NO_2. On the other hand, it is not in contradiction with the detonation studies presented earlier [37,38], where significant amounts of additive were required to effect changes in cell width. There seems to be a fundamental difference between the induction delay measurements and the detonation sensitivity measurements.

In Slutskii's model [39], he suggests that NO_2 reduces induction time by leading to a CH_3 oxidation channel:

$$\begin{aligned} &CH_3 + NO_2 \rightarrow NO + CH_3O \\ &NO + HO_2 \rightarrow NO_2 + OH \end{aligned} \tag{3.4}$$

As stated earlier, the importance of this path is a result of the importance of CH_3 in hydrocarbon oxidation, and the fact that it leads to chain termination in high temperature ignition (Westbrook [40]). A rapid oxidation path for CH_3 should therefore accelerate ignition kinetics, which should in turn reduce the characteristic detonation length scales. A more recent model resulting from the study of nitrate promoters in diesel fuel (Chan [54]) suggests the following paths:

$$\begin{aligned} &NO_2 + RH \rightarrow HONO + R \\ &HONO \rightarrow NO + OH \\ &2NO + O_2 \rightarrow 2NO_2 \end{aligned} \tag{3.5}$$

And:

$$\begin{aligned} &\mathrm{NO_2 + RH \rightarrow HNO_2 + R} \\ &\mathrm{O_2 + HNO_2 \rightarrow HO_2 + NO_2} \end{aligned} \qquad (3.6)$$

Where R is a fuel radical. However, both of these models require that either the HO_2 radical or O_2 be present to oxidize NO back to NO_2 or to strip HNO_2 of an H atom. This allows the NO_2 to act as a *catalyser* for ignition. Indeed, if trace amounts of additive are to play a major role, the effect should be catalytic, so that it may affect a significant number of elementary reactions without being rapidly consumed [55].

Slutskii [39] explains that the reactions that create HO_2 at lower temperature:

$$\begin{aligned} &\mathrm{HCO + O_2 \rightarrow CO + HO_2}, && k = 3.4 \cdot 10^{12} \\ &\mathrm{CH_3O + O_2 \rightarrow CH_2O + HO_2}, && k = 10^{12} \exp(-2250/T) \end{aligned} \qquad (3.7)$$

Are replaced by another set of reactions which become more rapid at higher temperature (> 1100-1200 K):

$$\begin{aligned} &\mathrm{HCO + M \rightarrow H + CO + M}, && k = 5.5 \cdot 10^{14} \exp(-8900/T) \\ &\mathrm{CH_3O + M \rightarrow CH_2O + H + M}, && k = 5 \cdot 10^{13} \exp(-10000/T) \end{aligned} \qquad (3.8)$$

Where k is the forward rate for each reaction and M is a non-reacting species. The dependence of the rate constants on temperature, according to the standard Arrhenius form, causes the switchover from reactions (3.7) to reactions (3.8) at the higher temperature ignition characteristic of a detonation. It is possible that the O_2 required in the second model proposed [54] (developed for diesel fuel ignition below 1000 K) is likewise not available at higher temperatures. The high temperature ignition typical of a detonation would therefore not benefit substantially from the presence of NO_2 as it would be consumed very rapidly. The results of Dorko *et al.* [44] mentioned earlier show that the reduction in the induction delay of $CH_4 - O_2$ when part of the O_2 is replaced with NO_2 is indeed less pronounced at higher temperatures. If this were the case, the small amount of NO_2 present in our experiments would be consumed in a negligibly small number of reactions, leading to an undistinguishable effect on the ignition kinetics, which would explain the absence of effect of NO_2 on run-up distance.

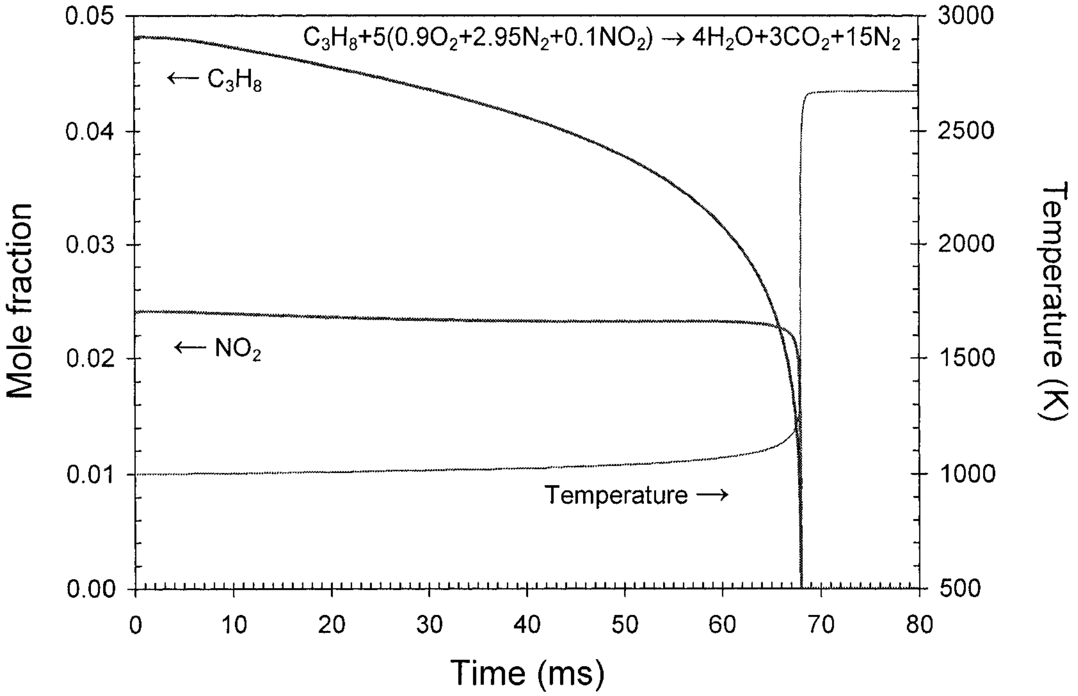


Fig. 3.9 Concentrations and temperature for low-temperature ignition

In order to verify the assumptions made above, simulated ignition experiments were run for the mixture with 0.5 NO_2-to-fuel ratio and $\beta = 3.0$ at two different temperatures. The low temperature case was at 1000 K (Fig. 3.9), and the high temperature case was at 1600 K, corresponding to the post-shock temperature for an ideal 1-D detonation in this mixture (Fig. 3.10). The kinetic mechanism used was supplied by Varatharajan [56] and includes 254 elementary reactions among 55 species. The code simulates a typical shock tube experiment by tracking the evolution of these species after they are suddenly brought to an imposed temperature. Both of the figures show the temperature evolution of the mixture and the evolution of fuel and NO_2 concentration. Ignition corresponds roughly to the inflection point in the temperature curve.

For the low temperature case, there is a gradual depletion of fuel while the NO_2 concentration and the temperature remain almost unchanged. Just prior to ignition, the fuel concentration actually drops below the NO_2 concentration. Finally, the NO_2 is

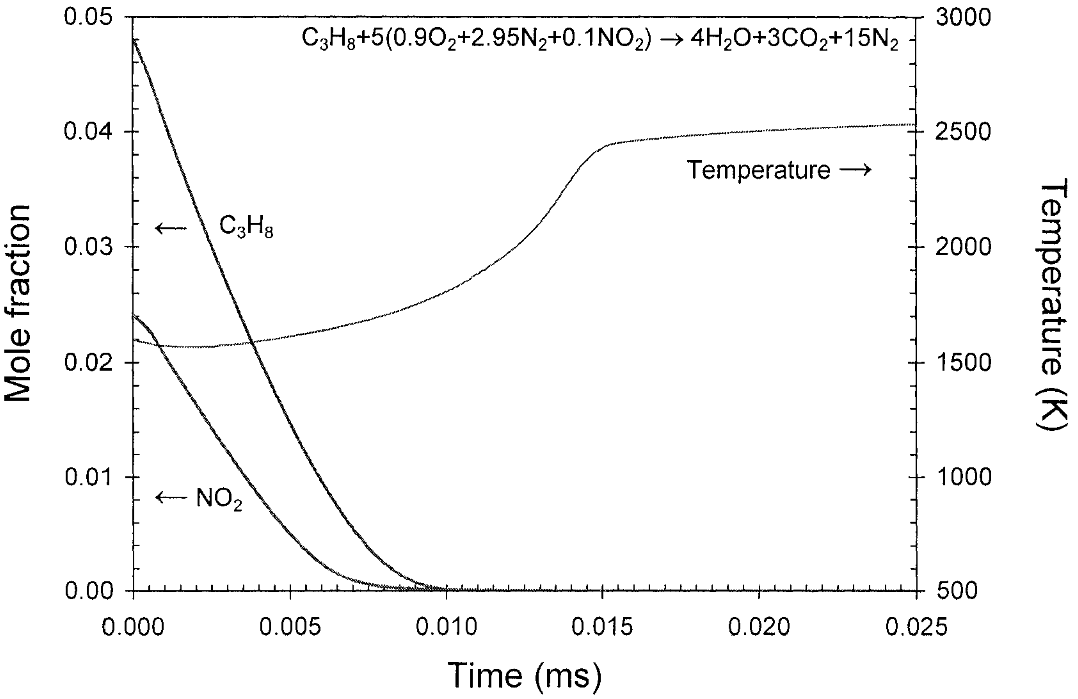


Fig. 3.10 Concentrations and temperature for high-temperature ignition

rapidly depleted as the temperature jumps by over 1000 K. The ignition time is roughly 68 ms. For the high temperature case, ignition is much more rapid (about 0.014 ms), so absolute times cannot be compared. However, it is interesting to note that in this case the NO_2 is depleted more rapidly than the fuel, so that it is no longer available for reactions like (3.4) through (3.6). While the actual mechanism has not been investigated, the effects seem to agree with the postulates made above. The means by which the NO_2 is depleted and the role it plays in initiating reactions with the fuel would require further study.

Chapter 4 Conclusions

The effects of acetylene and NO_2 on the detonation sensitivity of propane have been studied experimentally. The objective was to establish whether a small quantity of additive could sufficiently alter the kinetics of hydrocarbon – O_2 – N_2 mixtures to affect their detonability. The motivation for this work came from the need to significantly reduce the run-up distance to detonation in fuel-air mixtures for pulse detonation engines (PDE). Previous investigations showing significant reductions in induction delay of diesel and hydrocarbon fuels with small amounts of hydrocarbon or nitrate sensitizers indicated a promising route. Analysis of the results obtained with nitrates has allowed previous researchers to identify a path to sensitization dominated by the catalytic effect of NO_2 on the ignition kinetics of the fuel. More recent studies on the effect of nitrate sensitizers on the detonation characteristics of hydrocarbon fuels have indicated some effectiveness, but typically requiring a large amount of additive. This has made it difficult to evaluate the effectiveness of these compounds as sensitizers.

The investigation of the effect of C_2H_2 on $C_3H_8 - O_2 - N_2$ mixtures has shown that the effect is simply one of progressive "dilution" of one fuel with the other. The run-up distance varies gradually between that for each component. It is therefore not advisable to consider C_2H_2 as an additive for heavier hydrocarbon fuels.

This study has presented a method for comparing the sensitivity of fuel – O_2 – N_2 mixtures with and without NO_2 in such a way as to isolate the kinetic effects by eliminating energetic differences in the mixture. The experiments were carried out with mixtures of $C_3H_8 - O_2 - N_2$ and with NO_2 concentrations varying from 10% to 50% as compared to fuel concentration. Mixtures with identical energetics invariably displayed identical sensitivity as established by comparing run-up distance and cell size, indicating that the additives are not resulting in significant kinetic effects. This apparent contradiction with the previous work appears to be due to the temperature difference between typical diesel ignition and detonations. Above 1100-1200 K, the reactions that allow the catalytic effect of NO_2 seem to disappear.

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Appendix A Ion Probe Circuit

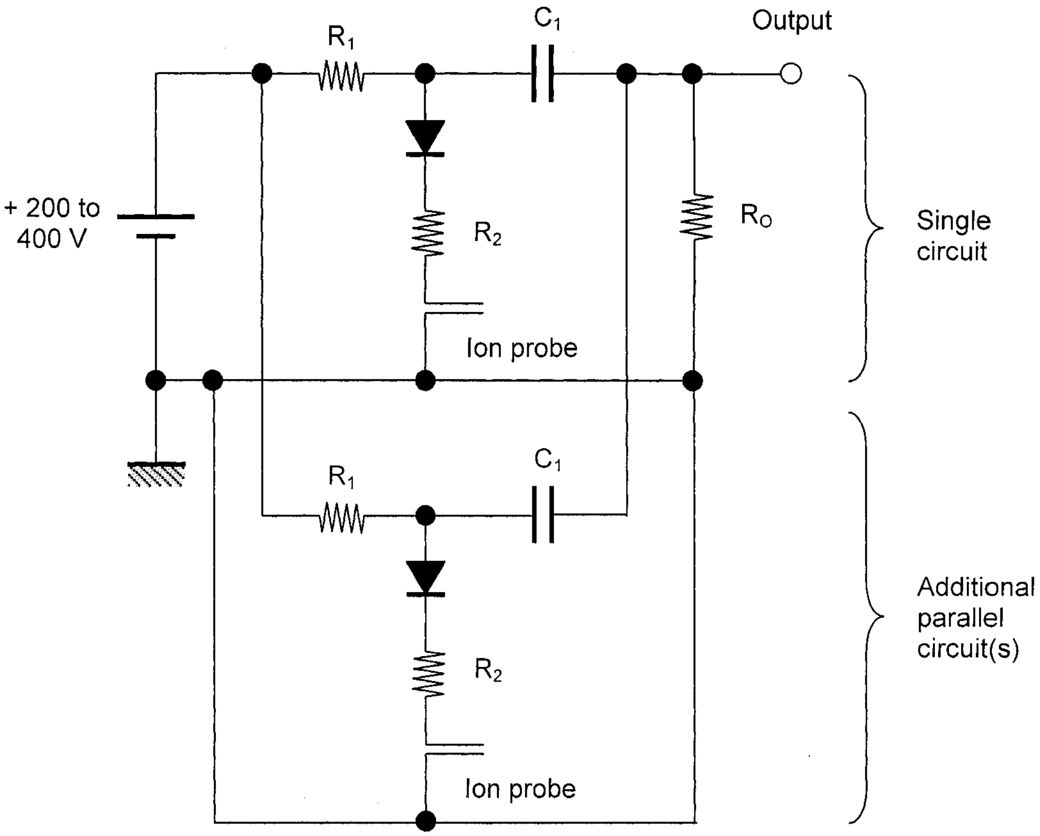

Fig. A.1: Ion probe circuit

R_1 (charging resistor) = 22 MΩ
R_2 (input resistor) = 10 kΩ
R_o (output resistor) = 3.3 kΩ
C_1 (capacitor) = 1 nF

A.1 Working Principle

Referring to Fig. A.1, the C_1 capacitors are charged through the R_1 resistors by the DC power supply. When the combustion wave passes across the ion probe, it becomes shorted (ideal case), resulting in the sudden establishment of a voltage across the output resistor R_o. This results in a spike at the output. The input resistor R_2 is used to reduce the noise, and thus smoothes out the output signal. Many of these circuits can be connected in parallel to a single output, provided there is enough temporal separation between signals. It was found that if a single circuit was used for all adjacent probes, the signals became difficult to isolate due to insufficient time for charging the capacitor. In this investigation, three circuits were staggered to provide temporal separation of the signals. Referring to Fig. 2.1, the first circuit contained the 1st, 4th, 7th, etc. ion probes, the second circuit contained probes 2, 5, 8, etc., and the third circuit contained probes 3, 6, 9, etc. In this way, each circuit was only solicited once for approximately every 0.45 m of travel of the combustion wave, leaving enough time for the capacitors to re-charge.