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High-Pressure Combustion and Deflagration-to-Detonation Transition in Ethylene/Nitrous Oxide Mixtures

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Nitrous oxide has been a compound of interest for the past several decades due to its exothermic decomposition. Currently nitrous oxide is used in a variety of industrial applications and is being investigated as a potential rocket propellant for next stage thrusters. Also, concerns about the safety of nitrous oxide have arisen in the nuclear industry, as it has been observed that stored nuclear waste generates high pressures of nitrous oxide with various gaseous fuels. Therefore, understanding the combustion characteristics, particularly under high pressure, of mixtures of fuel with nitrous oxide is highly important. The present work investigates the high pressure combustion characteristics of a stoichiometric mixture of ethylene and nitrous oxide ($C_2H_4 + 6N_2O$) in an alloy steel vessel with a 4 in. inner diameter and an internal length of 24.5 in. The combustion is initiated by energizing either a nichrome wire or an electric match connected to leads in the vessel. The experimental setup accommodates four high pressure (100,000 psia) transducers to measure pressure peaks at different points along the length of the vessel during the propagation of the combustion wave. Based on the time instants at which these peak pressures are recorded by the transducers it is possible to estimate the propagation speed of the combustion wave. The focus of this series of experiments is to investigate the dependence of combustion pressures, propagation speeds, and deflagration-to-detonation transition (DDT) on initial pressures of the above mixture of ethylene and nitrous oxide. Experiments were carried out at initial pressures of 100 psia, 125 psia, 150 psia, 200 psia, 337 psia, and 500 psia,. The preliminary 100 psia initial pressure tests were used to assess the correct functioning of all instrumentation. Overdriven detonations of different strengths were observed during each of the above tests. An overdriven detonation refers to the detonation process in which the main detonation parameters, such as detonation pressure and propagation velocity, exceed the corresponding CJ values. Along with this observation the transducers recorded elevated pressures, which were magnitudes in excess of the CJ values. The surprising experimental results are discussed and explained using theoretical considerations of flame acceleration, detonation, and DDT mechanisms.

1. Introduction

The decomposition and combustion properties of nitrous oxide (N_20) have been studied for nearly a century. Technical interest in nitrous oxide intensified in the 1960s because of the compound's positive heat of formation, and so heat is released during decomposition. Also, upon complete dissociation the products are pure nitrogen (N_2) and oxygen (O2).

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These characteristics made nitrous oxide a unique oxidizer for combustion systems, and ignited interest in using N2O in supersonic wind tunnels to increase the enthalpy. A great deal of work was done by the Air Force in the 1960s to characterize the decomposition and combustion of nitrous oxide. Laughrey et al. (1962) studied the decomposition and detonability of pure nitrous oxide at elevated temperatures and pressures, and while they were not able to achieve detonation but did observe high rates of chemical reaction they categorized as explosions. They concluded that it appears quite possible that a detonation wave in nitrous oxide can be established in a longer tube. In the next year, Jost et al. (1963) studied the detonation and chemical kinetics of hydrazine and nitrous oxide to assess the viability of N2O as an oxidizer for rocket combustion. They measured detonation speeds of hydrazine-nitrous oxide mixtures at very low initial pressures (on the order of 0.1 atm) and found the speed to be close to the ideal Chapman-Jouguet (CJ) detonation velocity. At the same time, Bollinger et al. (1962) were studying the detonation velocities and induction distances in hydrogen-nitrous oxide mixtures at initial pressures of 1, 5, and 10 atm. They ignited the mixtures in a tube with a 79 mm inner diameter by melting a copper wire, and then measured the speed of the propagating flame until it accelerated to the CJ detonation velocity. They found that the induction distance decreased with increasing initial pressure, and that at 10 atm the induction distance could be as small as 0.3 m.

In the past couple of decades, research on nitrous oxide has focused on the explosion hazard posed by fuel-N_2O mixtures, as N2O is used in a variety of industrial and aerospace applications. One particular area of concern is the handling and storage of nuclear waste, as it is known that the waste can generate combustible mixtures of gaseous fuel and nitrous oxide. To address this issue, Kaneshige and colleagues at the California Institute of Technology performed experimental studies of detonations in mixtures of fuels with N_2O, O_2, and N_2; they first studied detonations in hydrogen (H_2) and methane (CH_4) (1997) and then ammonia (NH3) (1999). The detonations were produced using direct initiation in a large (280 mm inner diameter, 7.5 m in length) detonation tube, and the detonation velocity and cell size were measured and compared with calculated theoretical values. Mével et al. (2009) and Bane et al. (2011) have recently studied the combustion characteristics of H_2-N_2O mixtures at low pressures, measuring the laminar burning speeds and comparing with chemical kinetics calculations. Finally, additional interest in nitrous oxide has arisen in the past several years as it is being more widely considered as a “safe,” clean oxidizer for rocket propulsion systems, as it is suitable as both a monopropellant or as a bipropellant (Merrill 2008). Recent accidents involving stored nitrous oxide have lead to concern over its explosion hazard, either from exothermic decomposition or through fuel contamination of stored N_2O creating an explosive mixture (Merrill 2008).

In the present work, the combustion of nitrous oxide with a simple hydrocarbon, ethylene, at high initial pressures is investigated. A series of experiments were conducted using a stoichiometric C_2H_4-N_2O mixture in a round, smooth-walled tube with initial pressures of 125 to 337 psi. A low-energy ignition mechanism (heated wire) to prevent direct initiation of a detonation, and the flame acceleration and subsequent deflagration-to-detonation transition (DDT) was observed. According to Joannon (1991), one of the critical parameters that determines the detonability of given gas mixture is the initial pressure, and so the effect of pressure on DDT was examined.

2. Methods

The experiments were performed at the High Pressure Lab at Purdue’s Zucrow Laboratories in a R4 reactor designed and manufactured by High Pressure Equipment Company. The reactor has an internal length of 24.5 in., inner diameter of 4.0 in, wall thickness of 2.0 in and is constructed of alloy steel (4340). The reactor vessel was designed for a pressure of 20,000 psia and hydrostatic pressure tested to 30,000 psia. As shown in Figures 1 and 2, the vessel has three ports on the side wall and one port through the cover (labeled 1 in Figure 1) to hold four PCB 109C11 pressure transducers. The transducers are connected to a high frequency data acquisition system via signal conditioning and record explosion pressures at these points in the vessel. Data is recorded at 600,000 samples/s/channel. The setup is equipped with plumbing to supply nitrogen from the high pressure supply and ethylene and nitrous oxide from respective bottles. The plumbing for the fuel and oxidizer includes separate sonic venturis that are used to set mass flow rates of the two gases resulting in the appropriate final pressure for each test. Nitrogen is used to pressure leak test and purge the vessel before and after every experimental run. The partial pressures of ethylene and nitrous oxide supplied to the vessel are calculated to achieve stoichiometric fuel-oxidizer mixture. The reactor is heated to approximately 100°F using strap heaters to prevent condensation at high pressures.

Ignition of the mixture is achieved using a heated nichrome wire in the end of the reactor. After setting up the nichrome wire and pressure leak checking before every test fire, the vessel is purged with nitrogen and nitrous oxide before pressurizing with ethylene and nitrous oxide to the calculated pressures. Pressurizing the vessel with ethylene and nitrous oxide is controlled by auto-sequence via a LabVIEW interface, and the gases are allowed sufficient time to mix before igniting the mixture.

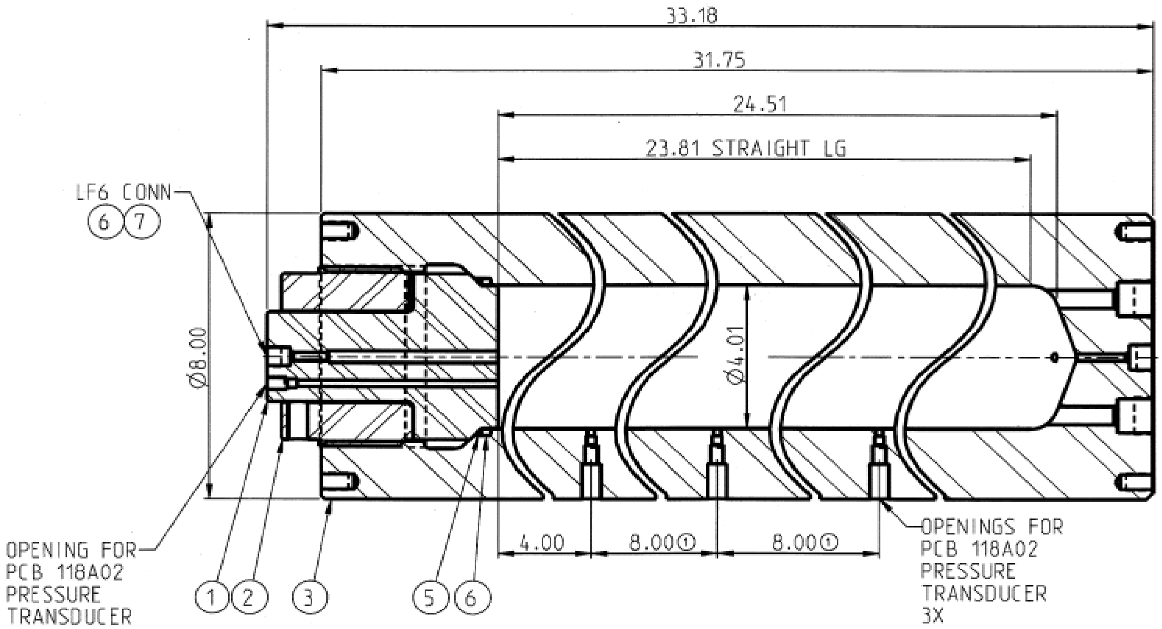

Figure 1: R4 reactor detonation tube specifications.

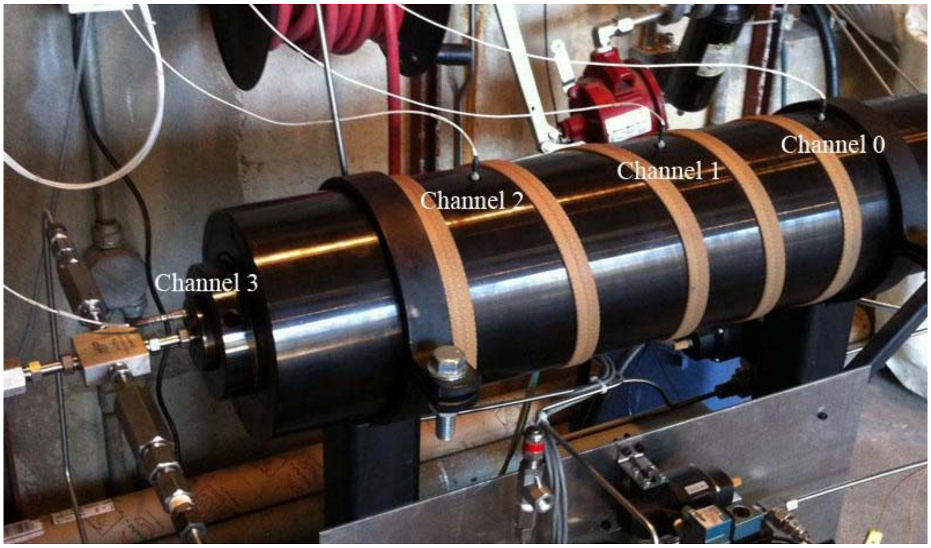

Figure 2: Experimental setup indicating locations of the pressure transducers.

For comparison with the experimental results, the CJ detonation velocities and CJ pressuresfor a stoichiometric C_2H_4-N_2O mixture at the elevated intial pressures were calculated. The calculations were performed using the Shock and Detonation Toolbox developed by Browne et al. (2005) at the California Institute of Technology. The toolbox works in Cantera, a suite of object-oriented software tools for problems involving chemical kinetics, thermodynamics and transport processes (Goodwin 2005).

3. Results and Discussion

Experimental runs with initial pressures 125 psia, 150 psia, 200 psia and 300 psia were conducted and the explosion pressures for each run are tabulated in Table 1. Based on the time instances of these pressure peaks and using the distance between transducers, the propagation speeds of the combustion waves were calculated and presented in Table 2. The CJ detonation velocities, D_{CJ}, corresponding to the different initial pressures, calculated using Cantera, are also given in Table 2. The pressure data logged from the transducers during each test were plotted versus time. The pressure vs. time for cases with 200 and 300 psi initial pressure are shown in Figures 3 and 4, respectively.. Note that in the plot for the test with initial pressure 300 psia, the pressure plot for the third transducer on the side wall failed to provide useful data and hence was not included in the tables.

Table 1: Combustion peak pressures as detected by the transducers.

Ex. No.	*Initial Conditions*		*Peak Pressures*			
	O/F	*Pressure (psia)*	*P_0 psia*	*P_1 psia*	*P_2 psia*	*P_3 psia*
30	9.55	125	12600.91	12669.91	16671.76	41316.46
31	-	150	13610.08	17888.93	14295.66	27628.52
32	-	200	24512.16	15406.14	29192.03	36350.60
33	8.82	200	12474.78	12222.93	13508.43	31326.93
34	9.33	337	36668.00	25338.16	-	61369.07

Table 2: Detonation velocities and overdriven factors

Ex. No.	*Initial Conditions*		*CJ velocity*	*Velocities & overdriven factors (D/D_{CJ})*			
	O/F	*Pressure (psia)*	*D_{CJ} m/s*	*D_0 m/s*	*D_1 m/s*	*D_2 m/s*	*D_3 m/s*
30	9.55	125	2279.19	85.32	2677.27	2736.65	1807.74
				0.0374	*1.1746*	*1.2007*	*0.7931*
31	-	150	2285.68	62.24	3328.41	2414.76	2090.19
				0.0272	*1.4562*	*1.0565*	*0.9145*
32	-	200	2295.78	74.83	3003.51	2798.91	1911.04
				0.0326	*1.3083*	*1.2192*	*0.8324*
33	8.82	200	2295.78	68.77	2239.12	2323.62	1807.76
				0.0299	*0.9753*	*1.0121*	*0.7874*
34	9.33	337	2309.59	85.65	2863.94	-	2293.96
				0.0371	*1.2400*	-	*0.9932*

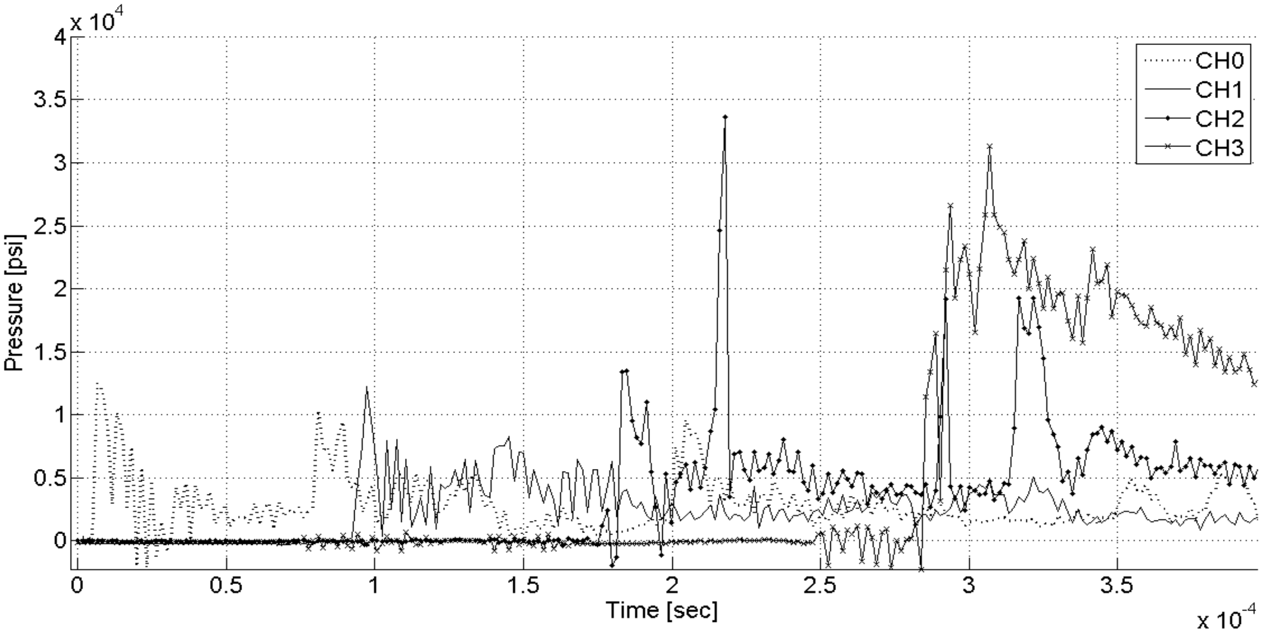

Figure 3: Pressure plots for 200 psia stoichiometric ethylene and nitrous oxide

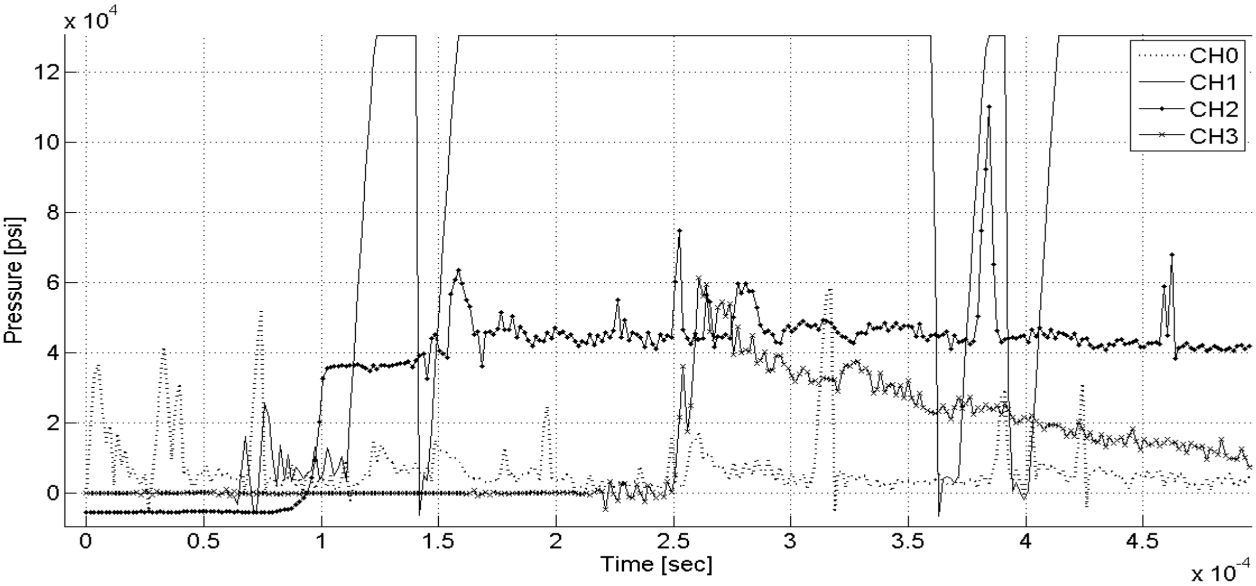

Figure 4: Pressure plots for 300 psia stoichiometric ethylene and nitrous oxide

The most striking result is the extreme high pressures recorded during the experiment. For the experiments, with the lowest initial pressure of 125 psi, the predicted CJ detonation pressure is approximately 5000 psi. However, the first transducer (p0) measures a pressure more than twice the CJ value, 12,600 psi. Similar results are also observed for the tests at higher initial pressures, with the measured peak pressure at the first transducer exceeding the predicted CJ value by a factor of 2 to 3. However, the average velocity of the combustion wave between the igniter and the first transducer was on the order of 90 m/s, well below the CJ detonation velocity. Since the energy of the igniter is far too low to directly initiate a detonation, it must first initiate a deflagration that then transitions to a detonation between the ignition point and the first transducer.

Lee (2008) discusses in-depth the mechanisms for deflagration-to-detonation transition (DDT) based on investigations of detonations in smooth tubes. In the current experiments, the mechanism is believed to be rapid acceleration of the deflagration immediately following ignition. Mixtures of fuels with nitrous-oxide can produce highly unstable and turbulent deflagrations that rapidly self-accelerate. For example, Bane et al. (2011) noticed that undiluted hydrogen-nitrous oxide flames became unstable nearly immediately following ignition, even at low pressures. Figure 5 shows a schlieren image of the flame in a lean H2-N2O mixture at an initial pressure of 5.8 psi, approximately 2.2 ms after ignition by an electric spark. The flame is highly turbulent, with wrinkles in the flame surface creating an elaborate cellular structure. This increase in the flame surface area causes a dramatic increase in the burning rate and hence the flame accelerates significantly. Therefore, a flame in a similar mixture like the one used in the present tests would likely also be unstable.

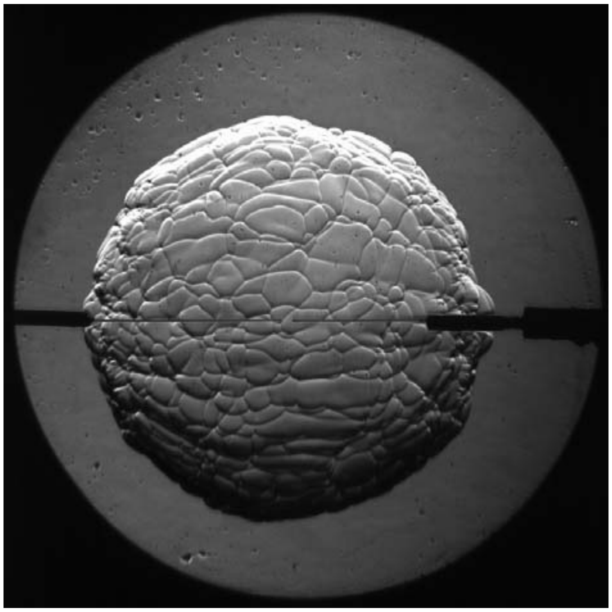

Figure 5: Schlieren image of an unstable hydrogen-nitrous oxide flame ($\phi = 0.4$, $P_i = 5.8$ psi).

The reactor used has a relatively small inner diameter (4 in.) and is only approximately 2 feet long (24,5 in. internal length) with a closed end, so the flame is highly confined. The turbulent flame emits pressure waves upstream that pre-pressurize the unburned gas. These waves reflect off the reactor walls and further interact with the flame front, magnifying the flame front turbulence and enhancing the flame acceleration. As explained by Lee (2008), if the flame acceleration mechanisms can bring the flame to a critical deflagration speed (usually on the order of half the CJ speed), the flame velocity will then accelerate rapidly and the flame will undergo transition to detonation. Depending on high the flame velocity is, DDT can spontaneously occur within a couple of tube diameters, as illustrated in Figure 6.

After the first transducer, the pressure changes moderately at the second (p1) and third (p2) transducers, but the average combustion wave speed is significantly higher, and in most cases larger than the CJ velocity. This suggests that the detonation is overdriven, with the overdrive factor (ratio of the velocity to the CJ velocity) also given in Table 2. Generally, an overdriven detonation is obtained from using extremely large ignition energy, i.e. an exploding wire that generates a strong overdriven blast wave. In this case, however, the ignition energy is far too small. A possible mechanism, as discussed by Lee (2008), is the generation of an overdriven blast wave by localized explosions. As the propagating deflagration front interacts with the reflected pressure waves in the vessel, the gas near the front is continuously compressed and heated, which can result in a localized explosion directly in front of the flame. This explosion creates a blast wave that will have a velocity significantly higher than a CJ detonation; as the detonation forms from the shock wave, it will initially be overdriven. Therefore, we postulate that in these experiments there occur one or more localized explosions near the deflagration front that result in an overdriven detonation wave. This would also explain the extremely high pressures, as even a small overdrive factor results in a dramatic increase in the detonation pressure. DDT is a very complicated, unpredictable phenomena, and this is further demonstrated by the significant variation in the pressures from one transducer to the next, as in the 337 psia initial pressure test, and between tests at the same initial pressure, as with the two tests at 200 psia. Such large varying in the pressure is not unexpected, given that the location and time of DDT is practically impossible to predict and is not repeatable, and thus is expected to change from test to test.

Finally, the fourth pressure transducer (p3) measures the reflected detonation pressure at the end of the tube. If the detonation reaching the end wall is in fact still overdriven as a result of the DDT mechanism, then the reflected pressures measured by the transducer are consistent with what the theory predicts. From the experiments conducted thus far, it appears that the high pressure, sensitivity of the flammable mixture, and the high level of confinement in the tube result in nearly-instantaneous DDT and a highly unstable, overdriven detonation reflecting from the end wall. According to Lee (2008), the overdriven detonation would decay in time to either a stable CJ detonation or an unstable detonation with a velocity oscillating around the CJ velocity. However, it appears that in these experiments the overdriven detonation does propagate a sufficient distance to decay to a near-CJ detonation.

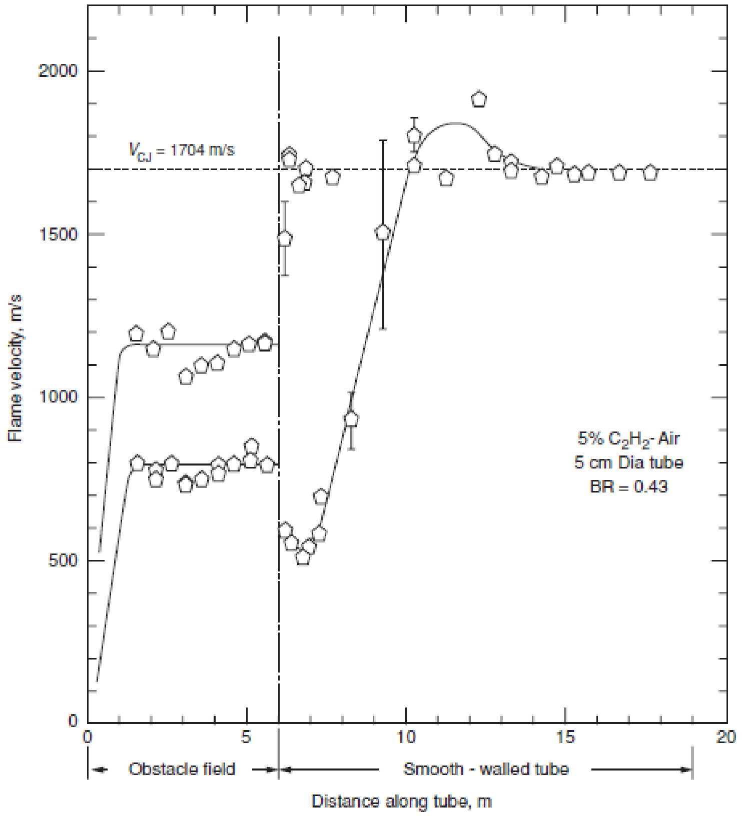

Figure 6: Example of deflagration-to-detonation transition in smooth tubes (Lee 2008).

4. Conclusions and Future Work

In all of the experiments conducted, deflagration-to-detonation (DDT) transition was observed and is believed to occur between the igniter and the first pressure transducer. In all cases, the pressures measured far exceeded the theoretical CJ detonation pressures. Given that the ignition energy is far too low to achieve direct initiation, the mechanism of DDT is believed to be rapid acceleration and self-turbulizing of the flame front coupled with compression by reflected pressure waves, leading to localized explosions. These explosions generate blast waves that eventually couple with a reaction zone to form a detonation. This theory helps to explain the very high pressures measured by the pressure transducers, as the blast wave will be highly overdriven compared to the CJ detonation, and therefore the pressures would be significantly larger. From estimates of the wave speed, it also appeared that, in at least part of the reactor, the velocity exceeded the CJ velocity, indicating an overdriven detonation. The rapid and violent DDT observed is caused by a combination of the mixture sensitivity, due to the nitrous oxide, the high initial pressures, and the degree of confinement inside the reactor.

The results of these experiments suggest that obtaining a stable detonation near the CJ point is not possible with this reactor, due its fairly small L/d ratio. The overdriven detonation wave does not have sufficient propagation distance to decay to a stable state, and therefore the reflected pressure measured at the end of the tube is much larger than the predicted reflected pressure. Therefore, we plan to continue this work in a second reactor with a very large L/d ratio to see if a stable detonation can be achieved and how it would compare to the theoretical CJ state. We also plan to use more instrumentation in the next reactor, including a larger number of pressure transducers as well as ion probes; these measurements will allow us to more accurately estimate the wave speed and to help identify when DDT occurs. In addition, we plan further tests in the existing reactor; first, more tests at the same initial pressures to determine the repeatability of the flame acceleration and DDT, and then further experiments with a range of off-stoichiometric mixtures to study the effect of fuel lean and fuel rich conditions on the mixture sensitivity. A theoretical study of the fuel-nitrous oxide mixtures and their predicted sensitivities (i.e. activation energy) and detonation characteristics will also be conducted simultaneous to the ongoing experimental work.

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