DETONATION AND SUPPRESSION OF DETONATION IN FUEL-AIR MIXTURES AT ELEVATED PRESSURES

by Thomas F. Seamans and Hans G. Wolfhard

Thiokol Chemical Corporation
Reaction Motors Division
Denville, New Jersey

INTRODUCTION

Gaseous detonations have been studied extensively and our basic knowledge of pressures in the detonation wave, its velocity and detailed structure is extensive. However, there is no way of predicting under what conditions a detonation rather than a deflagration will be established. This is no particular concern in fuel-oxygen mixtures as a detonation usually forms from a deflagration after a very short time period and distance from the ignition source. Fuel-air mixtures in contrast have seldom been observed to detonate although one would expect that given large and long enough vessels eventually detonation will occur. This has, in fact, been observed in natural gas and air mixture, where a detonation developed even at 0.4 atm initial pressure in tubes of 61 cm diameter and 93 meter length (ref. 1).

Detonations and the resulting high pressure peaks are a danger in many industrial applications. This experimental investigation was undertaken to assess the dangers of detonations or very high pressure peaks in large volumes containing fuel-air mixtures. Of special interest was the possibility of arresting detonations or deflagration by spraying into the tube large amounts of water. It was the original intention to conduct all experiments in a tube of 54.6 cm diameter and 9.45 m length that was designed to withstand high pressure. However, after initial experiments that lead to extremely high pressure peaks, it was decided to use this large tube for experiments at one atmosphere initial pressure only and to conduct detonation experiments at initial pressure higher than one atmosphere in a tube of smaller diameter but the same length as the large tube.

The experiments fall roughly into four categories.

A. Pressure dependence of fuel-air detonations.

B. Comparison of the onset of detonation in the large and small diameter tube.

C. The occurrence of autoignition in the large tube.

D. The influence of water curtains on explosions and detonations.

In A it was our intention to see whether fuel-air mixtures detonate at high pressure in systems where detonations do not occur at one atmosphere. Initial pressures were therefore raised up to 40 atm.

In B a comparison between the large and small diameter tube was made. As fuel-air mixtures did not detonate at one atmosphere initial pressure in either tube oxygen enrichment was used to induce detonation and the oxygen index was taken as measure for the ease with which a mixture would detonate.

In C a study was made of the very high pressure peaks that occur in regions where detonation is marginal. These peaks will be seen to be due either to pressure piling or autoignitions induced by forward or reflected shock waves.

In D the effectiveness of water curtains was investigated. These experiments were done in the large tube with oxygen enrichment. The sprays covered the whole cross section of the tube and the amount of injected water was extensive.

The instrumentation was restricted to high-speed pressure measurements. This allowed a full analysis of the pressure history in the tube but gave only indirect evidence of the position of the flame front. Surface thermocouples were tried to get this additional information but were not too successful, no doubt due to the fact that the flame front during the deflagration stage was highly turbulent and clear signals were not received, except when a detonation had been established.

EXPERIMENTAL APPARATUS

Two closed tubes of approximately the same length were employed in this investigation. A large tube, 54.6 cm in diameter, was used for the bulk of the tests at initial pressures of one atmosphere and for all tests in which water was injected into the path of a deflagration or detonation. A small tube, 38 mm in diameter, was used principally for tests at elevated initial pressures. Both tubes were equipped to accept piezoelectric pressure gages at various positions along the walls of the tubes. The locations of these stations and of the water injection ports are given in Table I and diagrammatically in Figure 1. Free stream pressures were measured with as many as eight Kistler SLM PZ 6 miniature pickups whose signals were displayed on oscilloscopes and recorded photographically. PC 6R Piezo-Calibrators were used with four of the pickups; PT 6R Amplifier-Calibrators were used with the other four. With the Amplifier-Calibrators, the response of the pickups is 150,000 cps; with the Piezo-Calibrators, the response is somewhat less. For tests in the smaller tube, adapters were necessary to extend the range of the gages to the much higher pressures produced by detonations at elevated initial pressures. These adapters reduce the response of the more sensitive gages to approximately 50,000 cps but have little effect on the response of the others.

Two four-beam oscilloscopes displayed the pressure signals and two high speed (1.53 meters/sec) streak cameras recorded them. A drum camera (12.7 meters/sec) was used for a very few tests but, though it provided more accurate wave velocity determinations, it was not possible to use the faster camera generally. The reason is that a history of the reflected waves was sought as well as of the incident wave and this would have resulted in double exposure of at least a part of the film. Consequently the Fairchild cameras were used in almost all of the runs. One millisecond timing blips were superimposed on the pressure traces, providing a time scale. A coil around a lead to one spark plug (see below) gave a signal, displayed on the oscilloscopes, indicating the capacitor discharge and therefore the start of a run on the film.

Considerable difficulty was encountered in attempting to load to one atmosphere the 2,130 liter volume of the large tube with a known uniform mixture of explosive gases. The first method was based on loading the previously evacuated tube by partial pressures and then mixing the gases with a blower in an external recirculation line. This method was found to be unsatisfactory due to the time required to achieve even a semblance of adequate mixing and due to air leakage into the system at the blower shaft during the long mixing times.

A revised system proved satisfactory and all tests discussed herein employed this system. In essence, the method was based on filling the vessel with the component gases premixed externally in the desired proportions in the flow system.

The large tube was evacuated to approximately 5 cm Hg absolute with an air ejector. The desired flowrates of air, oxygen (if required for the particular run), and fuel (methane, ethylene, or hydrogen) were established using calibrated orifices in which the flow was maintained critical. The three streams joined in a "mixer" from which one stream emerged at a pressure only slightly above ambient. This stream was vented to the atmosphere while the flows were being established; it then was allowed to flow into the large tube while the air ejector remained in operation. After a purge at low pressure for several minutes, the tube was permitted to fill to one atmosphere with the premixed gases. Samples of the final mixture in the tube and also of the emerging stream from the mixer were taken and subsequently analyzed by Orsat.

Ignition of the mixture at one end of the large closed tube was ensured by the use of three surface gap spark plugs, each with an independent capacitor circuit. The energy to which each capacitor was charged in all runs was 18 joules.

Loading of the 38 mm tube for initial pressures of up to 40 atmospheres was achieved in the following manner. A large tank was loaded with the desired gas mixture to one atmosphere in the same manner as the 54.6 cm tube (discussed above). The mixture in the large tank was then forced by water into the 38 mm tube. By this method, the tube was prepared for tests at initial pressures of from one to 40 atmospheres.

Ignition of the gas mixture in this tube was accomplished by the discharge of a capacitor (18 joules) across a surface gap spark plug similar to those used in the 54.6 cm tube.

Water injection into the 54.6 cm tube was through three poppets located on a spiral on the tube circumference. The distances between the spark plugs and the three spring loaded water injectors, which produce fine sprays, are given in Table I. For the runs with water injection, a 100 gallon tank was filled prior to the run. With a suitable delay mechanism, high pressure nitrogen was admitted to the water tank, forcing the water through the three poppets in the tube just prior to the spark. The delay period between water flow initiation and the capacitor discharge could be varied as desired.

RESULTS

High Pressure Data

In a closed steel tube 38 mm in diameter and 9.15 meters in length, a number of tests were made with fuel-air mixtures at initial pressures of 1 to 40 atmospheres absolute. The principal fuels employed were hydrogen, ethylene, and methane. For these tests, only mixtures of approximately stoichiometric proportions were used.

In no case was a detonation observed in any methane-air run. Even at the highest initial pressure tested, 40 atm, the wavelike pressure fluctuations within the tube were rounded. The maximum pressures recorded at any station for these methane-air runs were only two to three times the initial pressure.

Quite different results were obtained with the hydrogen-air and ethylene-air mixtures. For these mixtures, pressure ratios of about 15 for the former mixture and more than 20 for the latter mixture were recorded in some runs (Table II). These pressure ratios were caused by detonations. Pressure, however, could not be the sole criterion on which to base the description of the type of combustion. Average velocities of the pressure pulses between various stations along the tube-axis provide a better basis. The average velocities are plotted in Figures 2 and 3 for the hydrogen-air mixtures and the ethylene-air mixtures respectively. These velocities were computed from the measured time interval for passage of the pressure pulse between two successive stations at which the piezoelectric gauges were located. The average velocities so computed are plotted against distance from spark to the mid-point between the two appropriate stations as abscissa.

Two distinct regimes are evident in Figures 2 and 3; the lower corresponding to deflagrations or pressure pulses resulting from deflagrations, the upper to detonations. Clearly, detonations form in hydrogen-air mixtures at 6 atm initial pressure or above. For the ethylene-air case, 20 atmospheres appears to be the marginal initial pressure at which a detonation generally forms. Below 20 atm, detonations were not observed within the tube length.

The occurrence of a detonation is readily evident from Figures 2 and 3. However, they are misleading with regard to the location of the onset of detonation. The pressure-time records show that in those runs in which a detonation occurred, it was formed between stations 1 and 2 in every case. The pressures due to the incident wave passing station 2 are at least 10 times the initial pressure in all "detonation" runs as opposed to a maximum factor of 3 for the hydrogen-air "deflagration" runs and 7 for the C_2H_4-air "deflagration" runs (Table II). Additional evidence indicating detonation onset was between stations 1 and 2 is the fact that the records show the rate of pressure rise at station 2 was essentially infinite, as at succeeding stations, in detonation runs. In deflagration runs, on the other hand, the pressurization rates throughout were finite except at the far end of the tube where discontinuities of low amplitude were recorded. In hydrogen-air detonation runs, furthermore, no precompression of the unburned gas was observed at station 2 or at stations 6, 7, and 8 prior to the arrival of the pressure discontinuity. For the ethylene-air detonation mixtures, slight precompression at station 2 (from 20 atm initial pressure to about 28 atm) was recorded.

It should be mentioned that the average velocities for the intervals between stations 6 and 7 and also 7 and 8 lack precision mainly for two reasons. These intervals are 0.5 meters in length. For the highest velocities, therefore, the time differentials for traversal of the intervals by the flame front are of the order of 10^{-4} seconds or, for the camera employed, tenths of a millimeter of film. In addition, very high frequency oscillations were recorded at stations 6, 7, and 8 in many of the runs, particularly those in which detonations occurred. The amplitude of the oscillations prior to arrival of the detonation wave was generally very small; nevertheless, the precise instant of wave arrival was sometimes difficult to determine at stations 7 and 8. For these reasons, the average velocities between stations 6 and 7 and also 7 and 8 are subject to an error of up to 40% in runs in which detonations occurred. However, for the station 2 to station 6 interval, a distance of 4.5 meters, the average velocities are subject to an error of only about 5%.

The oscillations at 6, 7, and 8 referred to above made pressure determinations at these stations highly questionable in many cases. No values, therefore, are given for these locations in a number of runs. In some cases, a value is given preceded by the symbol "∼" to denote lack of precision due to the presence of the oscillations.

In several runs, one or more pressure traces went off the film. In these cases, the symbol ">" has been used in the tables before the number which corresponds to the maximum pressure able to be recorded at that station in the particular run. The true pressure may have been only slightly greater, or considerably greater, than the value reported.

Comparison of Detonation Runs in the Two Tubes

A series of tests were made at one atmosphere initial pressure in each of two closed tubes of approximately the same length. The large tube is 54.6 cm in diameter, the small tube 38 mm in diameter. The tests used fuel-air mixtures enriched with oxygen in approximately stoichiometric proportions. To describe the degree of air enrichment with oxygen, the parameter oxygen index is employed. Oxygen index is the ratio of moles of oxygen to moles of oxygen plus nitrogen. For air, O.I. = 0.21.

The results of the runs show that detonations are formed at lower oxygen indexes in the smaller (38 mm) tube. Table III presents the minimum oxygen indexes of approximately stoichiometric mixtures supporting detonations in each tube. The next lower oxygen indexes tested are also included. The significance of "autoignitions" reported in the table for some runs in the larger tube will be discussed in the next section.

Tables IV and V present pressure and velocity data of the incident waves for runs in the 38 mm tube and 54.6 cm tube respectively. Only runs in which detonations were formed are included for in these runs only could the location of the flame front at any instant be determined from the signals of the piezoelectric gauges. Runs in which water was injected into the path of a detonation wave are not given due to the interactions of the water curtain with the wave.

A comparison of the tables leads to some interesting observations. Practically without exception, the pressure due to the incident waves are higher in the larger tube. For the cases of hydrogen and methane, one might say this fact is due to the higher oxygen indexes in the larger tube. Surely, this is one consequence of a greater oxygen concentration necessary to induce detonation. However, the ethylene runs in each tube include similar oxygen indexes; and here also are found the higher pressures in the larger tube, regardless of which stations in each tube are compared.

The two tables also indicate that at least some degree of precompression occurred at some stations in the large tube prior to arrival of a detonation wave. No such pressure rises were recorded for the runs in the smaller tube. This, however, cannot preclude entirely the non-existence of precompression because of the reduced sensitivity (up to 1/5th) of the gauges in the smaller tube, necessitated by the fuel-air tests at higher initial pressures.

In addition to the pressure data, Tables IV and V give the average velocity of the flame front as it passes between various pairs of stations. From Table I, Locations of Stations, the distances between the spark and station 9, stations 9 and 10, and stations 10 and 11 in the larger tube are comparable respectively, to the distances between the spark and station 6, stations 6 and 7, and stations 7 and 8 of the smaller tube. The average velocities in these regions are plotted in Figures 4, 5, and 6 for the hydrogen, ethylene and methane runs respectively. It is evident from these plots that the average velocity of the flame front as it traverses the first 80% of the tube length is greater in the smaller tube for similar runs with the same oxygen index. For example, the average flame velocity in an ethylene run with an oxygen index of 0.37 was 722 meters/sec between the spark and station 6 in the smaller tube and just 380 meters/sec in the comparable distance in the larger tube. This trend is to be expected, however, as it leads to the previously stated fact that detonations are formed more readily in the smaller tube.

Further examination of Figures 4-6 indicates that the average velocity of the detonation wave in the subsequent 0.5 meter of the tube length is greater in the larger tube than in the smaller tube. Referring again to the ethylene runs with an oxygen index of 0.37, the average velocity between stations 6 and 7 in the small tube was 1670 meters/sec as opposed to 2270 meters/sec in the comparable region in the larger tube.

The data indicates, then, that for similar mixtures supporting detonations in each tube the average velocity of the flame front is greater in the smaller tube over the first 8 meters and then lower in the subsequent 0.5 meter distance. This is to be expected because the induction distance was found qualitatively to be shorter in the smaller tube than in the larger tube for the same test mixture. Consequently a stable detonation velocity would be approached earlier in the smaller tube; whereas, in the same region of the larger tube, the detonation velocity would still be significantly in the overdriven mode.

Occurrence of Autoignitions under Marginal Conditions

In addition to the deflagration and detonation processes on which the present work was based, a third phenomenon, termed autoignition, was observed in some runs in the 54.6 cm tube only. Invariably, the process occurred in the downstream end of the closed tube in the region of the conical frustum (Figure 1). In general, the phenomenon was observed in runs in which the oxygen index was between those supporting deflagrations and those forming detonations. Pressure disturbances from the accelerating flame front in such runs are comparatively strong. In fact, shocks were recorded in all "autoignition" runs just prior to the occurrence of the phenomenon.

The events leading to the autoignitions in all twelve such runs with the three different fuels can be classed as one of three types:

1. Double shocks of low strength which pass down the tube, are reflected, pass up the tube, are again reflected, merge into one shock, and pass down the tube for the second time. A second reflection at the downstream end of the tube, i.e. the region of the conical frustum, may or may not occur just prior to the large pressure "kick" of the autoignition. This mechanism was observed clearly in two ethylene runs and one methane run. All three runs had the lowest oxygen indexes for a particular oxygen-fuel ratio of any runs in which autoignition occurred. Table VI shows that the two ethylene runs of the type under discussion had compositions of O.I. = 0.29 with O/F = 2.3 and O.I. = 0.37 with O/F = 4.6. The methane run was for O.I. = 0.39 with O/F = 2.1. All runs with these fuels under conditions of similar oxygen-fuel ratios and lower

oxygen indexes resulted in deflagrations only.

2. Double shocks whose strengths are somewhat greater than those discussed above (i.e. pressure ratios of ~ 2.5 vs. ~1.8). In this case, the first shock of the pair is reflected at the downstream end of the tube and is then met near station 12 by the second shock traveling downstream. This mechanism was observed in four runs as indicated in Table VI.

3. A single shock of greater strength (pressure ratio ~ 3.5). Here, no reflected wave was recorded at station 12 prior to the sudden large pressure kick of the autoignition. Five runs exhibited this behavior.

Table VI indicates that the last two mechanisms occurred indiscriminately at oxygen indexes above those of (1) above.

The fact that the first large pressure "kick" appeared at station 12 in all runs is significant. Furthermore, the station 12 pressure-time trace recorded one or more small shocks, as described above, just prior to the sudden, large pressure rise. Consequently, the autoignitions occurred between station 12 and the end-flange in all cases. In a few cases, the phenomenon occurred practically at station 12. Here, the sudden pressure rise was not in the form of a discontinuity in the trace; rather, the trace showed a continuously increasing slope from essentially zero to infinity. This rounded nature of the trace corresponds to the period of rapid but finite build-up from ignition to nearly instantaneous explosion of the compressed mixture.

In the majority of runs, however, even the first large pressure kick, which was always recorded at station 12, was in the form of a discontinuity. In these runs, then, ignition occurred sufficiently downstream of station 12 to allow the resultant detonation wave, traveling upstream to overtake the pressure disturbances of the building-up process. The trace at station 12, therefore, recorded a discontinuity due to the resultant overdriven detonation wave. Although precise determinations were limited by the time resolution of the streak camera, an approximate average velocity of the overdriven detonation wave between stations 12 and 9 was 3000 meters/sec. The computation does not reflect the possibility that the overdriven detonation wave, traveling upstream, might enter before reaching station 9, the burned gas region behind the flame front propagating downstream from the spark ignition source.

The most striking effect of the autoignitions is the very high pressures generated from initial pressures of one atmosphere. These pressure peaks are greater by a factor of 2 or 3 than the pressures recorded in detonation runs due to the incident detonation wave traveling downstream. Pressure peaks of approximately 80 atmospheres were recorded in two methane runs due to autoignitions (Table VI).

Water Injection Tests

Several tests were made in the 54.6 cm tube with water injected into the path of a deflagration or detonation. Three poppets were used as injectors, producing a fine spray. The distances between the spark and the three water injection ports are given in Table I. The ports are located 120° apart on a spiral on the tube circumference. Each spring-loaded water injector has spray shields suitably oriented such that the major axis of the resulting elliptical hollow spray is normal to the tube axis. Since the angle of upstream penetration is approximately 20°, an atomized water curtain was produced whose thickness was more than 36 cm. Generally, the total water flowrate in each run was 51 kg/sec.

The presence of the water curtain had two principal effects. It either prevented ignition of the combustible mixture by the spark, or it slowed propagation of the flame front.

In nearly half of the runs made with water injection, no pressure rises were recorded and no audible evidence of an explosion was heard. Nevertheless, the capacitor discharge signal was recorded indicating that a spark did occur. It is believed that although a spark occurred, the mixture failed to ignite due to the presence of much water vapor and/or droplets in the immediate vicinity of the spark plugs. Qualitatively, the amount of water, for constant inlet flowrate, in the form of vapor and/or droplets in the immediate vicinity of the spark plugs may be expressed by the time delay between initiation of water flow and the discharge of the capacitors. This delay period was necessary due partly to the velocity of a flame and partly to the fact that up to 0.10 second elapsed between the beginning of flow through the poppets and attainment of steady state flow. The delay period, Δt, is included where known for the appropriate runs in Table VII. In general, the longer the delay period, the more likely ignition will not occur. However, runs 120, 130, and 133 (Table VII) are exceptions. It should be emphasized that the records indicate the combustible mixtures failed to ignite in such runs. There was no indication that combustion occurred in the tube section between the spark and the water curtain. The pressure records of station 2, which is located in this section, showed no pressure rises. In a few of these runs a surface thermocouple, whose response is equal to that of the pressure gauges, was located at station 1. The thermocouple, too, gave no indication of combustion in the tube between the spark and the water curtain. It must be inferred, then, that the injected water in no case extinguished a flame already established; rather, the water prevented ignition in such runs.

The second principal effect of the water curtain was to delay the propagation of a deflagration or detonation. Figures 7, 8, and 9 illustrate this fact graphically. High frequency oscillations which were generally recorded at each station after passage of a detonation wave have been omitted from the figures for purposes of clarity. These oscillations were usually of relatively low amplitude though occasionally they obscured, to some degree at least, subsequent pressure pulses. The reflected waves (see below) at station 12 of Figure 7 and at station 9 of all three figures were so affected and consequently their representations are less precise.

As indicated in Table I, the three water injection ports are located between stations 2 and 3. From Figures 7 and 8 especially, it is evident that the water curtain attenuated the shock recorded at station 2. If it is assumed that the first pressure disturbance recorded at station 3 (Fig. 7) is due to the shock at station 2, then the average velocity of the wave between the two stations is about 200 m/sec. Clearly, the water curtain not only attenuated the shock but also caused the wave to travel at an apparently subsonic velocity. The pressure traces at stations 4 and 9 give evidence that a flame emerged from the water curtain and subsequently accelerated to form a detonation between the two stations. The second peak at station 9 is due to the wave traveling upstream after being reflected off the closed downstream end of the tube. The reflected wave is seen at a later time at station 4, than at 3 and finally at 2. Between stations 3 and 2, the reflected wave was again attenuated as it passed through the water curtain.

Because a detonation was formed between stations 4 and 9 in this run, the double peaks, recorded on the station 4 trace between the incident and reflected waves, are believed to be due to a retonation wave. This wave has been partially overtaken by the reflected wave at station 3 and hence the latter wave was strengthened to the point of going off the film (indicated by the dotted lines). It is believed that the double peaks recorded on the station 4 trace are due to the three dimensional characteristics of the combustion in such a large volume. Inside a tube of 54.6 cm diameter, a deflagration wave traveling through a combustible mixture is not a plane surface but rather it advances as tongues of flame leap forward at various acute angles with the tube axis. Consequently, the pressure disturbances which result from these tongues of flame and which are propagated in all directions reach various points on a given circumference of the tube at different times. The waves are then reflected from the tube walls, interact, etc. In consequence of this behavior, a pressure transducer, which occupies but a small point on the large circumference of the tube, can be expected to receive multiple pressure disturbances as it is passed by deflagration or retonation waves. A detonation wave, because of its velocity, is more likely to be planar and therefore less apt to cause multiple pressure peaks as it passes a transducer.

DISCUSSION

Systematic studies of detonations in fuel-air flames have so far not been reported in the literature. However Bollinger, Fong and Edse (Ref. 2) found that hydrogen-oxygen flames, slightly diluted with nitrogen have a shorter induction distance from the spark to the onset of detonation at 5 atm initial pressure than at ambient conditions. Thus detonations seem to be induced more easily at high pressures than at 1 atm. It has now been established that hydrogen and ethylene-air mixtures will detonate given high enough initial pressure in tubes as short as approximately 10 meters. The reason for this fact is not entirely clear. A trivial explanation would be that at lower pressures the tube diameter (38 mm) is below the critical diameter necessary for detonation. This however overlooks the fact, as discussed below, that a small diameter tube may induce detonations more readily than a tube of large diameter. More significant is the fact that even at low pressure, deflagration or pressure pulses reach very high velocities that are normally the precursor of detonation. It is felt that the greater ease with which detonations are established at higher pressure is due to the slower dissipation of heat due to the higher density of the burnt gas. The way a deflagration forms a detonation can be described in general terms as follows: A laminar flame close to the spark is driven forward by the expansion of the burnt gases and gradually becomes highly turbulent. Very high velocities up to 1000 meters/sec are recorded during this stage. Shock waves are formed and partially overtake the flame front. These shock waves form a detonation rather suddenly, creating strong pressure pulses that are also transmitted through the walls of the steel tube and record on the pressure transducers. These pressure pulses in some instances allow to determine the accurate location of the onset of detonation. The burnt gases also will suffer heat losses due to conduction to the wall. It seems that a critical condition is reached at an early stage before the turbulent flame reaches high velocities. If the burnt gases cool fast enough at low pressure then the forward thrust of the flame front will not reach the value necessary to create the turbulent flame that in turn reaches the very high velocities. The creation of the fast turbulent flame will therefore depend on pressure that controls the dissipation of heat of the burnt gases, and on the fundamental burning velocity which controls (together with the forward movement of the gas) the flame speed. This explains the greater ease with which hydrogen-air forms the fast turbulent flames than ethylene-air. In methane-air the very fast flames were never observed.

A second critical condition not yet fully understood is the ease with which a detonation forms from shock waves. This condition may be related to spontaneous ignition with short induction period. In general terms the formation of a detonation thus would depend on two conditions; one relates to the formation of very fast turbulent flames that will create shock waves, the second concerns ignition from shock waves.

Methane-air flames have a smaller burning velocity than ethylene-air flames, but the reduction is rather minor when one considers the differences between hydrogen and ethylene. It is therefore a surprise that methane-air flames do not give rise to detonations at 40 atm; in fact the deflagration is so mild that pressure ratios are very small and much less than theoretical. At one atmosphere the rate of heat dissipation is comparable to the formation of heat in the flame front, thus a fast flame never materializes in a tube of small diameter. At high pressure it has been found that the fundamental burning velocity of methane-air is greatly reduced (Ref. 3), and is only about 6 cm/sec at 40 atm. Thus again no fast turbulent flame will form. Methane-air flames seem to be unique in that increased pressure does not promote detonation. In general, it is felt that increased pressure has an influence on the first conditions (fast turbulent flame) for detonation rather than on the second (formation of detonation from shock waves) as shock waves of a given pressure ratio will lead to nearly identical temperature increases independent of initial pressure.

It is also interesting to note that detonations always occurred between stages 1 and 2; thus either detonation sets in relatively early or not at all. It is therefore questionable whether hydrogen-air would detonate in a tube of 100 meters length and 38 mm diameter at a lower pressure than in the 10 meter long tube.

In making a comparison between the data on the large and small tube it has to be realized that practically all data were taken in a region where detonation is marginal. Thus no stable detonation velocities are established as yet, detonations may be overdriven and overpressures may be present. This region is of little interest theoretically but of great interest practically as all fuel-air detonations are marginal.

Originally the comparison between small and large tube was made to ascertain that the high pressure data discussed above are meaningful, i.e. may be applicable to the large tube. The oxygen index was thus chosen for a comparison. It was quite unexpected to find that detonations need a higher oxygen index in the large tube than in the small one.

The course of events from spark to detonation as sketched before helps to understand the phenomenon. The early slow flame and its burnt gases will expand into three dimensions rather than only into one direction as in the small tube. Thus accelerations are smaller and a fast turbulent flame will form later or not at all within the given geometry. This qualitatively explains the slower original velocities and the higher oxygen indices necessary for detonation in the large tube. Shock waves formed in the turbulent flame will not only move forward but undergo multiple reflections on the walls and be more subject to attenuation before they can cause a detonation.

Overpressures and overdriven detonations have been observed before but have not been extensively studied. They are of great importance if one considers the safety of containers where explosions or detonations may occur. The present data allows a closer analysis of these phenomena. Little evidence of overpressures is found in the small tube, whereas truly astonishing pressure ratios are found in the large tube. It seems that two phenomena contribute to the large pressures observed and both can only occur in marginal detonations. In the first case a detonation develops so late in the tube that the unburnt gas was already precompressed before the detonation reaches the end of the tube. Evidence of this precompression has been found; it has, however, to be pointed out that events under conditions of marginal detonation are not very reproducible. Also the pressure transducers had to be calibrated to read up to 100 atm thus a precompression of one or two atmospheres is difficult to detect on the records. As detonations developed in the small tube always very early, the detonation could overtake the precompression wave and no overpressures are possible.

A second cause of overpressures is due to the reflection of shock waves at the end of the tube with possible contributions from the adiabatic compression in the tapered end section of the large tube. Ignitions have been observed due to incident, reflected and double shock waves. In each case the ignition occurs in precompressed gas, thus leading to overpressures. The largest pressure ratio observed being 80.

It was hoped that powerful water curtains would cause deflagrations or detonations to die out or at least to moderate appreciably the pressure peaks in the vessel. This was not found to be the case. Details of the events in the water curtains are fully discussed in the previous paragraph.

Finally it may be mentioned that the very high pressure peaks could be fully substantiated by strain gage measurements on the outside wall of the large vessel.

Acknowledgments

The authors wish to thank Messrs. A. H. Clark and R. H. Tromans for conducting the experiments and Mr. J. Macatician for many valuable discussions. This work was supported by the U. S. Navy under contract NOas 60-6047c.

REFERENCES

1. Gerstein, M., Carlson, E. R., and Hill, F. U., Ind. Eng. Chem., 46, 2558-62, (1954).

2. Bollinger, L. E., Fong, M. C., and Edse, R., WADC Technical Report 58-591, August, 1959 (ASTIA Document AD 239 677).

3. Wolfhard, H. G., The Burning Velocity of Methane Flames at High Pressures, Trans. Farad. Soc., 52, 1, 1956.

4. Bone and Townend, Flame and Combustion in Gases, Longmans, Green and Co., London (1927).

TABLE I. LOCATIONS OF STATIONS AND WATER INJECTION PORTS

	DISTANCE FROM SPARK, meters	
STATION	54.6 cm TUBE	38 mm TUBE
1	1.00	0.80
1a		1.53
2	1.48	3.30
3	2.49	5.31
4	3.50	6.30
5	4.00	7.30
6	5.01	7.80
7	6.01	8.30
8	7.01	8.80
9	8.01	
10	8.51	
11	9.01	
12	9.51	
End-Flange	9.85	9.15
WATER INJECTION PORT		
1	1.79	
2	1.97	
3	2.15	

TABLE II

INCIDENT WAVE DATA FOR FUEL-AIR MIXTURES IN 38 mm TUBE

INITIAL PRESSURE Atm. Abs.	O/F	RUN NO. 10B-1-X-	PRESSURE AT STATION (Atmospheres Absolute) 1	1a	2	6	7	8	AVERAGE VELOCITY BETWEEN STATIONS (Meters Per Second) 0-1	0-1a	0-2	1-2	1a-2	2-6	6-7	7-8	CHARACTER OF REACTION
H_2-Air																	
2	0.56	194		6.9	3.3	5.4	7.5	4.6		218			805	715	715	715	Deflagration
4	.59	195		14.3	11.7	14.3	18.5	24.2		268			843	865	834	1000	Deflagration
6	.52	155	18.8		63	56	50		320			1000		1690	1850		Detonation 1-2
10	.52	176	35.8		82	110	~92		400			834		2140	1670		Detonation 1-2
20	.51	182	52		~242	~324			216			758		1800			Detonation 1-2
20	.48	175	66		~145	~210			308			1040		2420			Detonation 1-2
C_2H_4-Air																	
6	3.0	171			42	41	37	43			168			865	910	910	Deflagration
10	3.6	158			32	~82	~67				88			704	834		Deflagration
14	3.4	196		25	43	82	59	43		109	194		590	764	556	556	Deflagration
17	3.3	197			92	~205				153	264		708	1000	1250	833	Deflagration
20	3.0	164			122	~390					127			1050	1000	1250	Deflagration
20	3.2	178				~330					162			2040	2000	2000	Detonation 1-2
20	3.2	170				>370	>400	>450			147			~2250			Detonation 1-2
20	4.8	160			>120	>170	>190	>350			254			~2250	~2500	~2500	Detonation 1-2
30	3.3	198			~330						275						

TABLE III

MINIMUM OXYGEN INDEXES OF MIXTURES AT ONE ATMOSPHERE SUPPORTING DETONATIONS IN EACH TUBE (ALSO NEXT LOWER O.I.'S. TESTED)

	54.6 cm TUBE				38 mm TUBE			
FUEL	O.I.	O/F	ONSET (DISTANCE FROM SPARK) Meters	RUN NO. 10B-1-X-	O.I.	O/F	ONSET (DISTANCE FROM SPARK) Meters	RUN NO. 10B-1-X-
H_2	0.30	9.53	3.5 - 8.0	113	0.23	0.56	3.3 - 7.8	149
	.25	.55	Deflagration	53	.21	.49	Deflagration	156
C_2H_4	0.37	3.4	1.5 - 4.0	97	0.30	3.5	0.8 - 3.3	148
	.34	3.3	3.5 - 8.0	133*	.21	3.2	Deflagration	177
	.33	3.1	Autoignition	96				
	.30	3.6	Deflagration	95				
CH_4	0.52	1.8	1.5 - 4.0	85	0.32	2.2	3.3 - 7.8	142
	.48	2.5	Autoignition	90	.29	2.3	Deflagration	150
	.47	2.1	Autoignition	124				
	.45	1.8	Deflagration	84				

* Water injection occurred in this run.

TABLE IV

INCIDENT WAVE DATA FOR MIXTURES AT ONE ATMOSPHERE IN 38 mm TUBE[(a)]

O.I.	O/F	RUN NO. 10B-1-X-	PRESS. AT STATION (b) 2	6	7	8	AV. VELOCITY BETWEEN STATIONS 0-6	6-7	7-8	0-2	2-6	CHARACTER OF REACTION
			Atmospheres absolute				Meters per second					
H_2												
0.23	0.56	149	9.5	17.1	~15		354	1670		166	2040	Detonation 2-6
.26	.57	139	8.5				~500			250	~1900	Detonation 2-6
C_2H_4												
0.30	3.5	148	14.3	19.7	14.5	~13.4	406	1670		192	2250	Detonation 1-2
.32	3.4	145	21.6	18.8	15.0		600	1670		311	1875	Detonation 1-2
.37	3.5	146	17.3	16.4	13.8		722	1670		384	2040	Detonation 1-2
.45	3.5	147	20.5	17.0	14.8		1040	2000		590	2370	Detonation 1-2
CH_4												
0.32	2.2	142	7.7		13.1		291	1000	1520	150	938	Detonation 2-6
.36	2.4	143	7.8		12.1	~15.7	481	1000	1250	270	1140	Detonation 2-6
.42	2.4	144	9.9		~12		~620	~1670		344	~1550	Detonation 1-2

(a) Only runs in which detonations were formed are given. Data for flame front of deflagration runs cannot be obtained from the pressure transducers alone.

(b) Pressure changes due to incident wave at station 1 were negligible or so slight that error is disproportionate. (Any rises were very gradual).

No precompression was observed prior to arrival of wave at any station in any run.

TABLE V

INCIDENT WAVE DATA FOR MIXTURES AT ONE ATMOSPHERE IN 54.6 cm TUBE[a]

O.I.	O/F	RUN NO. 10B-1-X-	PRESSURE AT STATION 2	PRESSURE AT STATION 5	PRESSURE AT STATION 9	PRESSURE AT STATION 10	PRESSURE AT STATION 11	PRECOMPRESSTION AT STATION 5	PRECOMPRESSTION AT STATION 9	PRECOMPRESSTION AT STATION 10	PRECOMPRESSTION AT STATION 11	AV. VELOCITY BETWEEN STATIONS 0-9	AV. VELOCITY BETWEEN STATIONS 9-10	AV. VELOCITY BETWEEN STATIONS 10-11	DETONATION ONSET BETWEEN STATION
			Atmospheres Absolute					Atmospheres Absolute				Meters per Second			
H_2															
0.30	0.53	113			~28				3.8	3.3	3.6	294	2270	1610	4 - 9
.31	.57	54			22				3.6	3.1	4.5	307	3120	2380	8 - 9
.33	.56	55	1.6	10	19	17.4	20.7	1.4	1	1	1	504	2170	1720	2 - 5
.40	.57	56		19	16	12	18.5	1.6	1	1	1	611	2270	1670	2 - 5
.40	.58	111	2.1		21	13.4			1	1		585	2270		2 - 3
C_2H_4															
0.37	3.4	97		28.6	24.7	24.8	26.5	1.6	1	1	1	380	2270	1610	2 - 5
.38	3.6	109			>34.7	35			5.6	5.1	3.0	276	3120	1850	3 - 9
.43	3.5	98		26.8	28	28	22.9	1	1	1	1	581	2380	2380	2 - 5
CH_4															
0.52	1.8	85	2.1		33.3	28.8	24.9	1.6	1	1	1	469	1850	2080	2 - 5
.56	2.5	91	1.9	24.7	~26.5	~21	~18.4	1.4	1	1	1	413	2000	1785	2 - 5

(a) Only runs in which detonations formed are given. Data for flame front in deflagration runs cannot be obtained from the pressure transducers alone. Same is true for runs in which autoignition occurred.

TABLE VI

AUTOIGNITION RUNS IN 54.6 cm TUBE

								MECHANISM	
FUEL	O.I.	O/F	RUN NO. 10B-1-X-	PRESS. DUE TO LAST SMALL SHOCK @ 12 ATM. ABS.	IDEAL TEMP. DUE TO LAST SMALL SHOCK @ 12, CALC. °C	PRESS. DUE TO AUTOIGN. PULSE @ 12 ATM. ABS.	DOUBLE SHOCKS, TWO PASSES	DOUBLE SHOCK SINGLE PASS.	SINGLE SHOCK SINGLE PASS.
H_2	0.32	0.34	80	6	117	~ 60		x	
C_2H_4	0.29	2.3	101	~14		>30	x		
	.33	3.1	96	13.7	332	>57		x	
	.38	3.3	108*	7		>57			x
	.37	4.6	105	~12		>56	x		
CH_4	0.39	2.1	72	~17		~80	x		
	.45	2.3	118*	7.2		>53			x
	.47	2.1	124	~23		~66		x	
	.47	2.2	114*	8		>52			x
	.48	2.2	120*	6		>57			x
	.48	2.5	90	11.5	307	>61		x	
	.56	2.7	86	6		~77			x

* Water injection occurred in these runs.

TABLE VII

SUMMARY OF WATER INJECTION RUNS AND SIMILAR RUNS WITHOUT WATER INJECTION

FUEL	O.I.	O/F	RUN NO. 10B-1-X	H_2O FLOW RATE Kg/Sec	Δt - TIME BETWEEN H_2O INITIATION AND SPARK Signal, Sec.	CHARACTER OF REACTION
H_2	0.21	0.52	126	51	0.86	Apparently no Combustion
	.21	.53	135	51	—	Apparently no Combustion
	.21	.54	52	a		Deflagration
	.21	.63	136	a		Deflagration
	.21	.67	137	51	.25	Deflagration
	.29	.51	131	51	~.8	Apparently no Combustion
	.29	.53	130	51	~.8	Detonation 4 - 9
	.30	.54	112	51	—	Detonation 4 - 9
	.30	.53	113	a		Detonation 4 - 9
	.33	.56	55	a		Detonation 2 - 5
	.37	.59	110	51	.21	Detonation 0 - 2
	.40	.57	56	a		Detonation 2 - 5
C_2H_4	0.21	3.1	134	51	—	Apparently no Combustion
	.21	3.3	127	51	.86	Apparently no Combustion
	.23	3.1	93	a		Deflagration
	.33	3.1	96	a		Autoignition
	.34	3.3	133	51	~.8	Detonation 4 - 9
	.37	3.4	97	a		Detonation 2 - 5
	.38	3.3	107	48.5	.13	Autoignition
	.38	3.6	109	a		Detonation 3 - 9
	.39	3.3	108	51	.17	Autoignition
CH_4	0.32	2.1	71	a		Deflagration
	.32	2.3	132	51	—	Apparently no Combustion
	.35	2.8	89	a		Deflagration
	.36	2.3	115	51	.20	Deflagration
	.37	1.8	83	a		Deflagration
	.39	2.1	73	48.5	—	Apparently no Combustion
	.39	2.1	72	a		Autoignition
	.39	2.2	116	a		Deflagration
	.45	1.8	84	a		Deflagration
	.45	2.2	117	51	.25	Apparently no Combustion
	.45	2.3	118	51	.28	Autoignition
	.47	2.1	124	a		Autoignition
	.47	2.2	114	51	.19	Autoignition
	.48	2.2	120	51	~.8	Autoignition
	.48	2.5	90	a		Autoignition
	.49	2.1	119	51	.37	Detonation 4 - 9
	.56	2.5	91	a		Detonation 2 - 5
	.57	2.1	51	36	—	Detonation 0 - 2

a - No water injected in these runs.

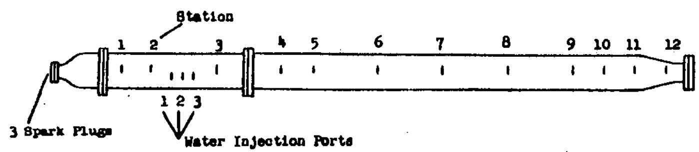


Figure 1(a). Diagram of 54.6 cm Tube

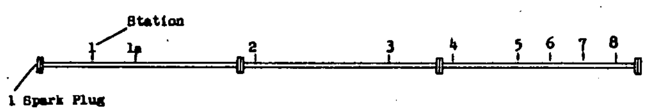


Figure 1(b). Diagram of 38 mm Tube

FIGURE 2. EFFECT OF PRESSURE ON HYDROGEN-AIR MIXTURES (38 mm TUBE)

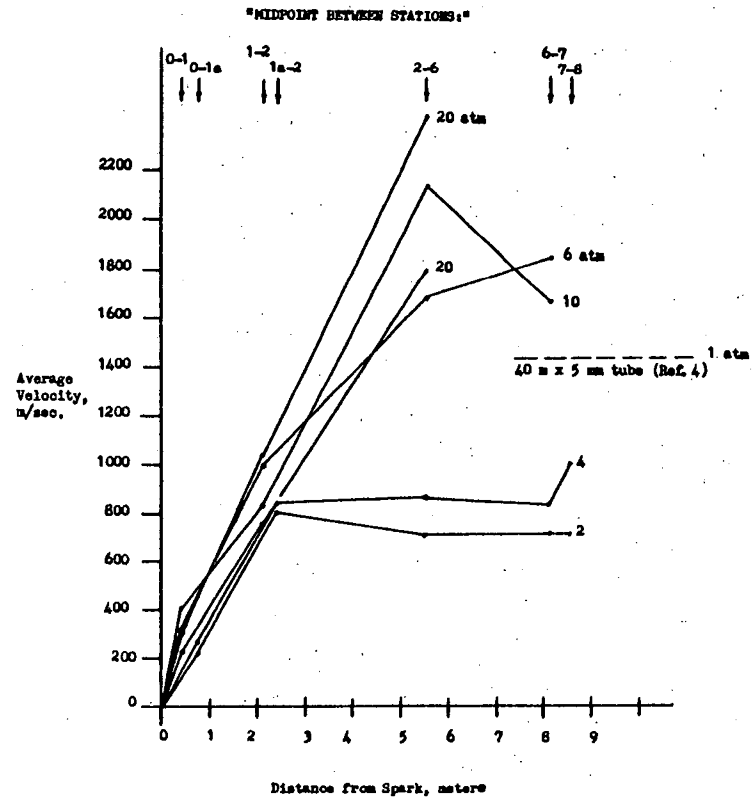


FIGURE 3. EFFECT OF PRESSURE ON ETHYLENE-AIR MIXTURES (38 mm TUBE)

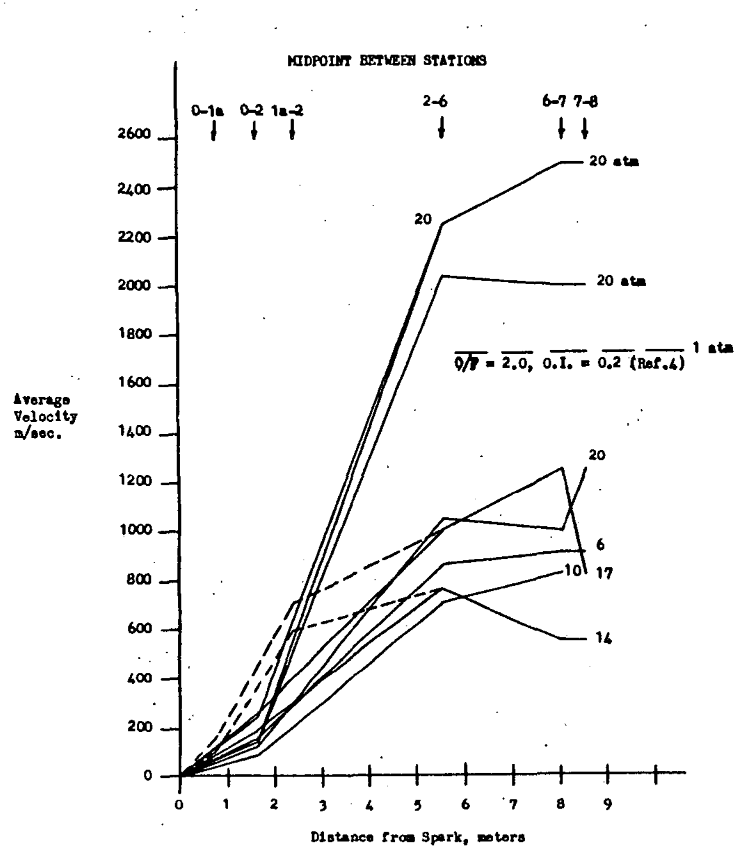


FIGURE 4. HYDROGEN-"ENRICHED AIR" RUNS IN BOTH TUBES AT ONE ATMOSPHERE

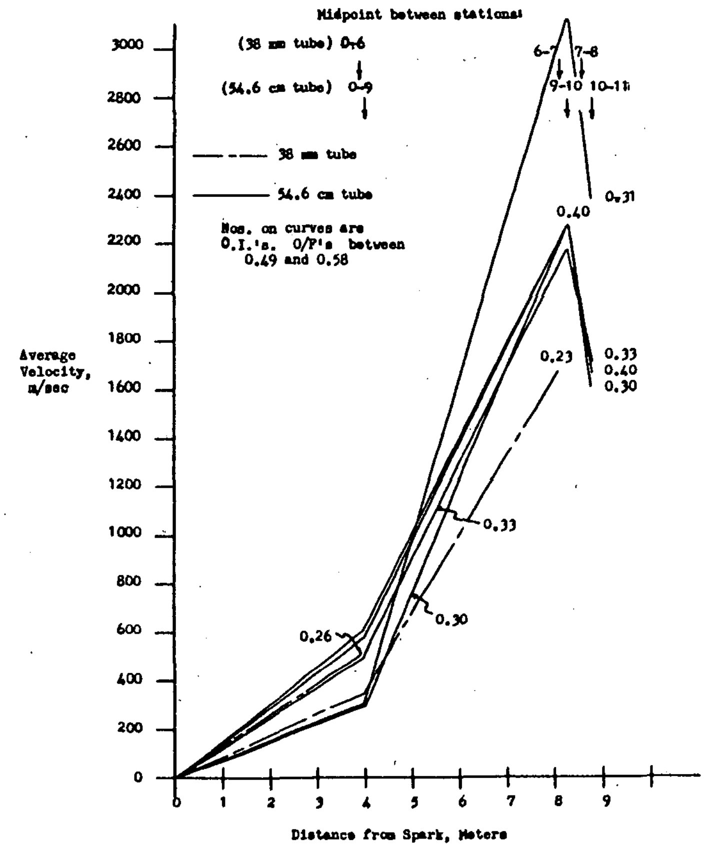


FIGURE 5. ETHYLENE-"ENRICHED AIR" RUNS IN BOTH TUBES AT ONE ATMOSPHERE

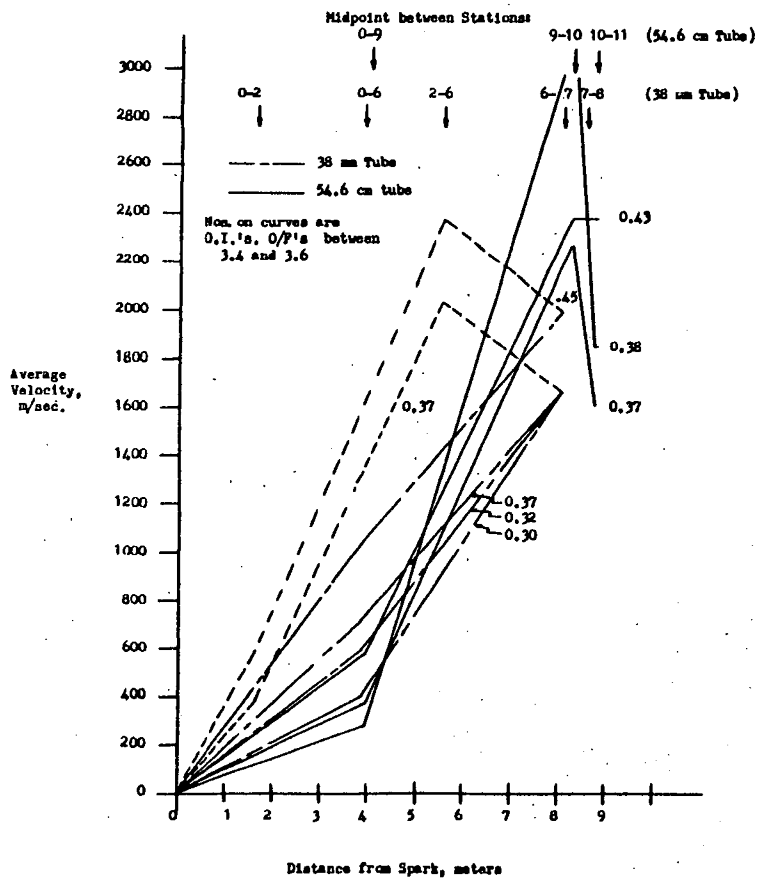
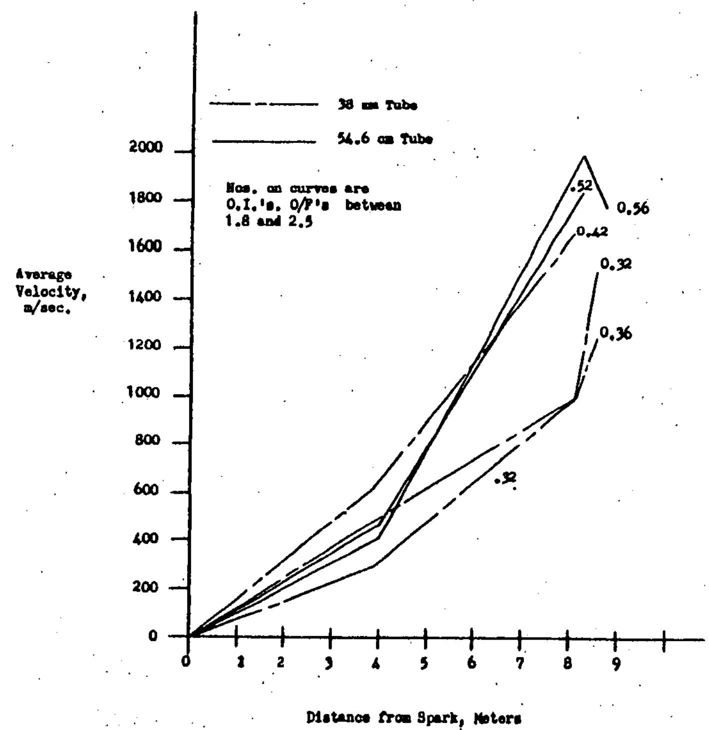


FIGURE 6. METHANE-"ENRICHED AIR" RUNS IN BOTH TUBES AT ONE ATMOSPHERE



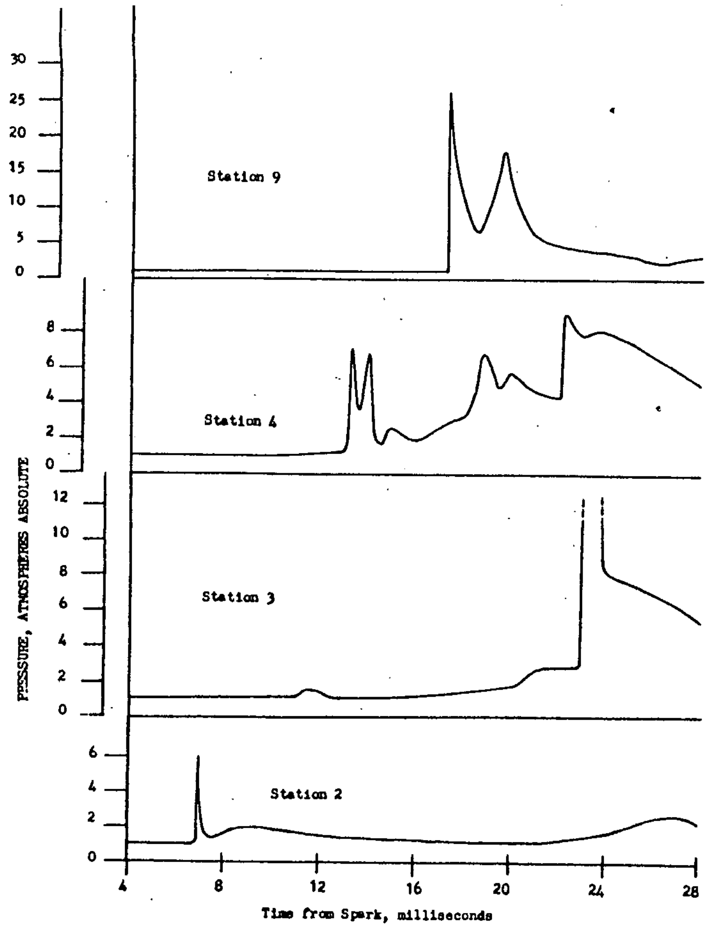


FIGURE 7. PRESSURE-TIME TRACES OF H_2-O_2-N_2 RUN (#112) WITH WATER INJECTION

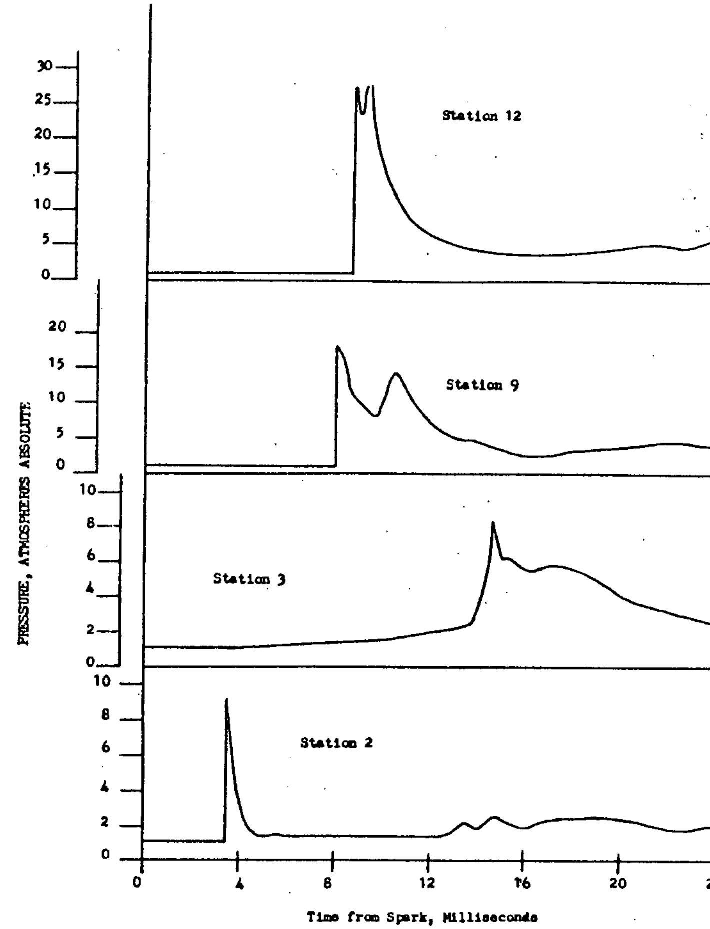


FIGURE 8. PRESSURE-TIME TRACES OF H_2-O_2-N_2 RUN (#110) WITH WATER INJECTION

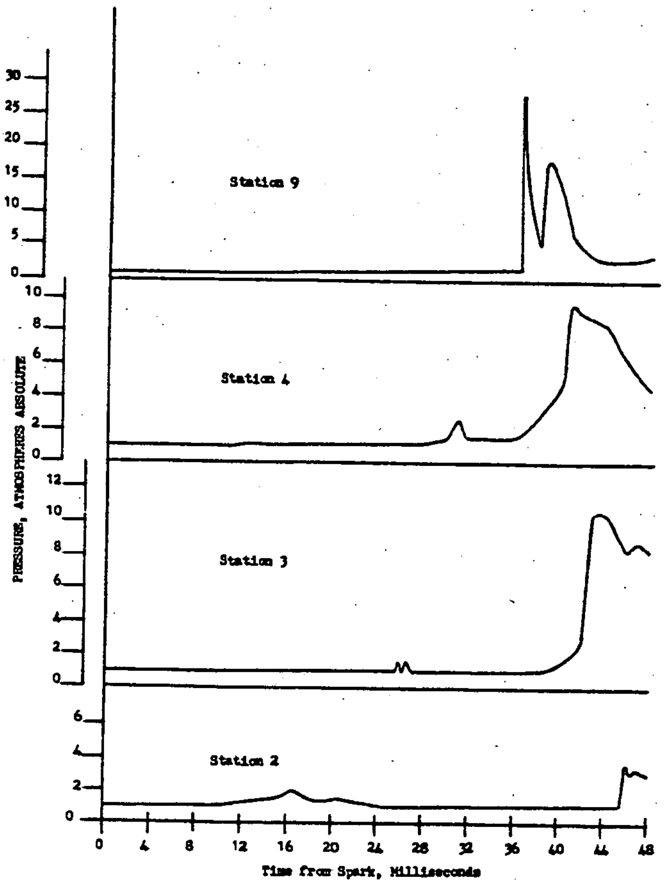


FIGURE 9. PRESSURE-TIME TRACES OF CH_4-O_2-N_2 RUN (#119) WITH WATER INJECTION