THE EXPLOSIVE DECOMPOSITION OF ACETYLENE IN PIPELINES

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SYNOPSIS

Studies of the self-decomposition characteristics of acetylene in pipelines have been made as a function of tube diameter, initial pressure, energy of initiation and diluent concentration. Detonation limits have been determined.

Velocity measurements indicate that detonation in acetylene is an unstable phenomenon. The evidence suggests that pressures developed during detonation, especially at the end of a pipeline, can be up to an order of magnitude greater than those predicted from classical theory.

Introduction

Acetylene is an important industrial raw material which, because of its ability to decompose explosively in the absence of air, is subject to statutory control under the Explosives Acts. For many years this laboratory has been required to answer questions concerning the safe storage, transport and use of acetylene and it is from this viewpoint that experimental work has been undertaken.

When undiluted acetylene is ignited in a tube, progressive decomposition may or may not occur depending on the state of the system. If the rate of energy release does not exceed the rate at which heat is lost the decomposition will die out; if it is in balance, the reaction proceeds slowly; if it is in excess, the preheating and precompression of the acetylene may lead to the formation of a shock wave and finally to detonation.

For a given tube condition the decomposition behaviour depends markedly on the initiation energy and the rate of its release. The upper limiting experimental case is provided by detonative ignition applied to the whole cross-section of the tube. Over-excitation may occur, but in a tube of sufficient length the effect is temporary and the reaction will either reach a steady state or die out depending on the initial pressure of the acetylene and the tube geometry. The lower experimental limit is the case where either the energy released or the rate of energy release into the system is insufficient to support an expanding reaction zone in the acetylene. Again this is dependent on the initial pressure of acetylene and the tube geometry.

The behaviour of acetylene has been examined in pipelines of various diameters over a range of initial pressures using several types of initiation. It has been found that in a system capable of sustaining detonation, the energy used to initiate decomposition determines the behaviour in the predetonation regime and the pressure developed when detonation is established. This level of energy is of great importance in practice because for reasons of capital cost, the design strength of a plant is limited to that required to withstand pressures predicted by the classical detonation theory for the Chapman–Jouguet plane. Although every effort is made to eliminate all possible sources of initiation in plant design, it is important that length to diameter ratios of any free space within vessels in the plant are such that transition from deflagration to detonation cannot occur.

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In this paper some of the more important work carried out in this laboratory over the past few years has been reviewed. The first half of the paper is devoted to a discussion in general terms of the results that have been obtained, including the effect of diluents, on the progressive decomposition of acetylene, and the second half to a discussion in more detail of the results of the work carried out in 12·7 and 305 mm internal diameter tubes. These latter experiments were done as a direct result of problems of hazard assessment posed by industry.

Review of Previous Work

Kogarko, Lyanin, and Mikailov,[1] using acetylene in a 360 mm bore tube, found that on changing from hot wire ignition to 200 J spark ignition, the pressure limit for detonation fell from 322 to 191 kN/m^2 abs. By using much more vigorous initiation, explosion can be set up at much lower pressures. Using powerful detonators, Bone and Fraser[2] set up explosive decomposition of acetylene at room temperature and pressure in 25 and 13 mm diameter tubes, although the decomposition appeared to be decaying. Duff, Knight, and Wright[3] produced sustained detonation in acetylene in a 23 m length of 12·7 mm diameter tube at 80 kN/m^2 abs. using tetryl as the initiator. At Woolwich, using 61 m of 305 mm bore tube, it was found that the pressure limit for deflagration using 200 J exploding wire ignition was 100 kN/m^2 abs. whereas a propagating detonation occurred down to a pressure of 50 kN/m^2 abs. when high explosive initiation was used. It appears that acetylene is unique in that it is able to propagate a detonation at initial pressures below those at which it is capable of sustaining deflagration.

Rimarski[4] and Boesler,[5] using short vessels, found that the minimum pressure for explosive decomposition of acetylene decreased with increasing vessel diameter. The minimum pressure was approximately 200 kN/m^2 abs. in a vessel of 40 mm diameter, and decreased asymptotically to 150 kN/m^2 abs. at a vessel diameter of 250 mm. An even more marked dependence on diameter of the limiting pressure for progressive decomposition was found by Sargent[6] in his work with long pipelines. The limit was approximately 200 kN/m^2 abs. in 40 mm diameter tubes, but fell to about 100 kN/m^2 abs. in 250 mm diameter tubes.

Several studies have been made of the factors influencing the distance travelled by a deflagration wave prior to its transformation into a detonation wave. Miller and Penny[8] and Hölemann, Hasselman, and Dix[9] have shown that in

narrow pipes the predetonation distance decreases with increasing pressure. On the other hand Shuey[10] found that in tubes of diameter 6·4 to 114·3 mm with acetylene at several initial pressures and fuse-head ignition, a detonation wave formed after the deflagration had travelled a distance equal to 60 tube diameters into the initially quiescent gas. He also found that when certain obstructions were placed in the tube near the ignition source, the distance to detonation was abruptly reduced in all cases by a factor of 12. Shchelkin[11] studied the predetonation regime in tubes roughened by the insertion of a wire spiral and obtained results in qualitative agreement with those of Shuey.

Detonation pressure ratios can be calculated from classical detonation theory.[12, 13] For gaseous acetylene, the pressure normal to the walls of the containing vessel is calculated to be 40 to 45 times the initial pressure in the "von Neumann Peak " and 20 to 25 times the initial pressure in the " Chapman–Jouguet Plane " neglecting the dynamic factor in each case. When the detonation meets a head-on obstruction, such as the end of the tube, there is a reflected shock wave and the pressure rises another 2 to 2·5 times. This pressure is exerted on the walls near the end of the tube as well as on the end itself. It lasts longer in a long tube than it does in a short one and the destructive effect is 40 to 45 times the initial pressure. Such computed pressures have limited use in practice since pressures many times greater have been observed. The actual pressures achieved depend on factors relating to the setting up and the degree of stability of the particular detonation.

Kogarko[14] using an acetylene/air mixture at 100 kN/m² abs. destroyed the end of a 305 mm bore firing tube previously tested to 20·3 MN/m² abs. This led him to carry out a controlled investigation with propane/air mixtures in which the pressure and the composition of the gas in the tube were fractionally below that required for detonation to be achieved. A ballistic pendulum was used to measure end pressures; ratios of end pressures to initial pressures of up to 470 : 1 were recorded.

Rimarski[15] working with acetylene in a 100 mm bore tube 30 m long at initial pressures of 163 to 191 kN/m² abs. using fused wire ignition found that detonation occurred at the end of the pipe. Destruction of the end of the tube occurred frequently and terminal pressures of 35 to 60 MN/m² abs. were measured. In 300 and 400 mm bore pipes, with acetylene at 152 kN/m² abs., pressures of 35·4 MN/m² abs. were measured and the ends of the pipes were petalled.

Two explanations have been put forward to explain the magnitude of these end pressures. Sargent[16, 17] considers that when deflagration occurs in a pipe of limited length, since it travels at less than sonic velocity, the pressure of all the gas in the pipe rises continuously as the reaction progresses. When the deflagration accelerates to become a detonation the unburnt gas is then at a higher pressure than initially, and the pressure reached in the Chapman–Jouguet Plane is therefore 20 times this enhanced pressure, and up to 50 times this enhanced pressure at the end of the tube. He uses this concept to explain why pressure rises by factors exceeding 100 and even 200 have been measured. The predetonation distance of travel of the decomposition zone lies within a range dependent on the initial pressure and the tube diameter; the greater the fraction of the tube length covered prior to the onset of detonation, the greater the pressure rise. Oppenheim[18] suggests that over-driving on transition to detonation occurs as a result of the incipient detonation catching up with the precursor shock front. This gives rise to much higher pressures than those predicted from classical theory. If this transition occurs near to the end of the tube, the destructive effects are much greater than predicted.

Work published by Ivanov and Kogarko[7] has thrown some doubt on whether the cascading process proposed by Sargent is the explanation of these high terminal pressures. It was found that the pressure at the end of the explosion tube, where the detonation wave was reflected, was always the same for a given initial pressure, in spite of the fact that the distance for transition from deflagration to detonation was a variable.

Although much work has been done on the stabilisation of acetylene with inert diluents, it has been mainly confined to experiments using small pressure vessels.[5, 19] Ammonia[20] and carbon monoxide[21] have been shown to have good stabilisation effects, but apart from these it is apparent that even at heavy dilution it is not possible to suppress completely the hazard of explosion and operate at a high partial pressure of acetylene. The effects of diluents on the progressive decomposition of acetylene in pipelines has been considered only by Miller and Penny,[8] and they believe that detonation remains a hazard even at appreciable dilution if the length to diameter ratio is high enough.

Decomposition of Undiluted Acetylene

In this laboratory, the criterion used for the onset of detonation in acetylene has been based on practical observation. It has been noted that in cases where the time/distance data have indicated the formation of a detonation wave, an examination of the sensing probes after firing has shown that a sharp change from unbent to fully bent probes had occurred in the region of the transition. Comparison of the angles of bending of the probes with the time/distance data suggests that the probes become fully bent as the velocity exceeds approximately 1500 m/s. Therefore, the distance to detonation has been defined as the distance to the first fully bent probe, or the distance for the velocity of propagation to reach 1500 m/s. This criterion appears to set a lower limit for detonation velocity in acetylene for which there is no justification, especially in view of some of the results obtained in the 12·7 mm tube work; however, in cases where there is a run up distance to detonation, it does serve as a useful baseline for comparison purposes.
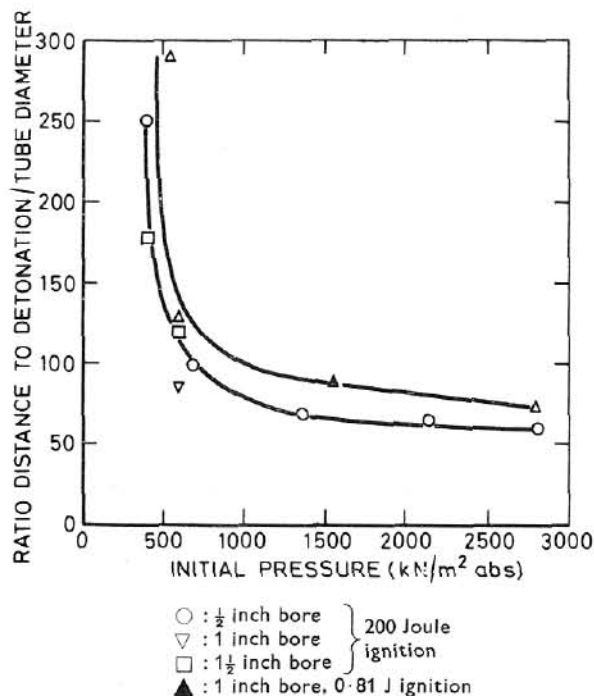

Fig. 1.—Acetylene. *Distance to detonation as a function of initial pressure and tube diameter*

The decomposition of acetylene has been studied in tubes 13, 25, 38, 152, and 305 mm diameter, of lengths 16, 30, 20 and 30, 13, and 61 m respectively. Special steel tubing, cold drawn or hot finished, with 35/41 UTS has been used. Except in the case of the 305 mm tube investigation, where ionisation probes were used, the probes were of the metal bridge wire type.

Distances to detonation found in 12·7, 25·4, and 38 mm tubes using 0·81 J and 200 J fusing wire ignition are shown in Fig. 1 as a function of initial pressure and tube diameter. Although only two energies of initiation have been used, it does appear that *inter alia* the greater the energy of initiation, the shorter is the run-up distance to detonation at any particular initial pressure. In general, the results indicate that as the initial pressure of acetylene is increased, the run-up distance to detonation decreases and approaches a limiting value of 60 times the tube diameter. This conclusion is in limited agreement with the findings of Shuey who, although quoting a figure of 60 times the tube diameter for the run-up distance, found that it was not pressure dependent. On the other hand, work on combustible mixtures (*e.g.*, with air and oxygen) of other gases shows that run-up distances are pressure dependent.[22, 23]

Velocities of detonation in undiluted acetylene induced by exploding wires and gaseous detonations of oxygen/acetylene mixtures are shown as a function of tube diameter and pressure in Fig. 2. In the case of gas initiated propagation in the 12·7 mm tube, average velocities of less than 1500 m/s were recorded, the criterion that has been used as the minimum velocity for a propagating detonation to form from a deflagration. Although the information does not extend to high pressures at large tube diameters, the available results indicate that the velocities form a family of curves and that the velocity of detonation increases as the tube diameter increases at a particular initial pressure. From theoretical considerations Zeldovitch and von Neumann have predicted a linear relationship between velocity of detonation and the reciprocal of pipe diameter. Results at two pressures are plotted in this manner in Fig. 3 and they confirm the prediction and give a limiting value for the velocity of detonation in tubes of infinite diameter of approximately 2100 m/s. Penny[24] calculated a velocity of
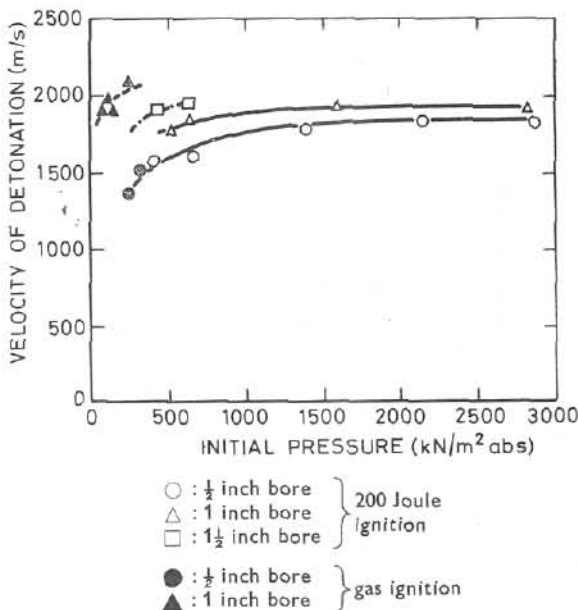

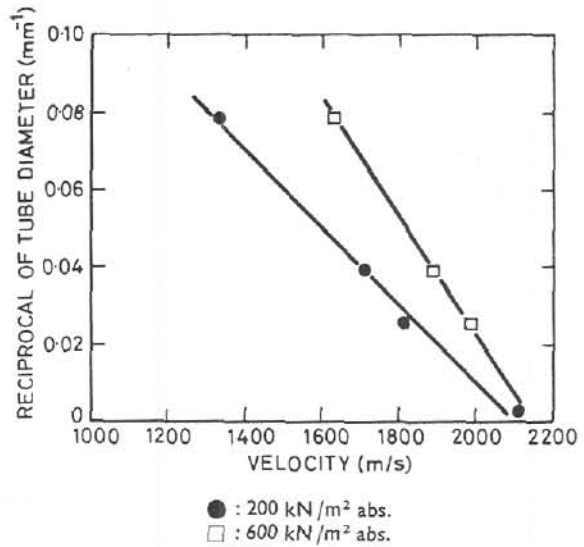Fig. 3.—Acetylene. *Velocity of detonation as a function of the reciprocal of the tube diameter and the initial pressure*

● : 200 kN/m² abs.
□ : 600 kN/m² abs.

2053 m/s for acetylene at an initial pressure of 800 kN/m² abs. from classical theory, which is in good agreement with the extrapolated value.

Although propagating decomposition of acetylene occurred in the 13 m length of 152 mm diameter tube, steady state detonation was not achieved. Between the 4 m and 11 m probe stations, the velocities of decomposition varied between 0·5 m/s at 100 kN/m² abs. and 600 m/s at 400 kN/m² abs., the highest initial pressure investigated. From Fig. 1 it can be estimated that the run-up distance to detonation at 400 kN/m² abs. in such a tube would be 200–300 tube diameters, that is 60–90 m, hence, the 13 m length of tube used was not long enough for stable detonation to become established. However, in the experiment at 400 kN/m² abs., there was an end effect which damaged the end of the tube, although this had been designed to withstand much greater pressures than those predicted by classical detonation theory. This effect is almost certainly due to a transition to detonation in the last few mm of the tube as a result of pressure piling.

Effects of Diluents on the Decomposition of Acetylene

The effects of nitrogen, ammonia, and carbon monoxide on the detonation limits and the deflagration limits of acetylene in a 31 m length of 38 mm diameter tube have been studied at pressures up to 600 kN/m² abs. Ignition was achieved by a discharge of a nominal 200 J through an explodable wire. The results are shown in Figs 4, 5, and 6.

The volume percent of nitrogen required to quench detonation varied between 0 at 250 kN/m² abs. and 30 at 600 kN/m² abs. (Fig. 4). Below the region of detonation, deflagration occurred over a range of nitrogen concentrations with velocities of propagation down to 0·2 m/s. The nitrogen content required to prevent propagation completely was in the region of 46–51 % v/v at 600 kN/m² abs.

For ammonia (Fig. 5) both the limits for detonation and deflagration were at lower percentages of diluent. At 600 kN/m² abs., the limits were approximately 20% and 30% for detonation and deflagration respectively. In the region of deflagration, velocities of propagation were again found to be down to 0·2 m/s. However, the region of deflagration was far less well defined than in the case of nitrogen.

In the case of carbon dioxide (Fig. 6), similar results to those
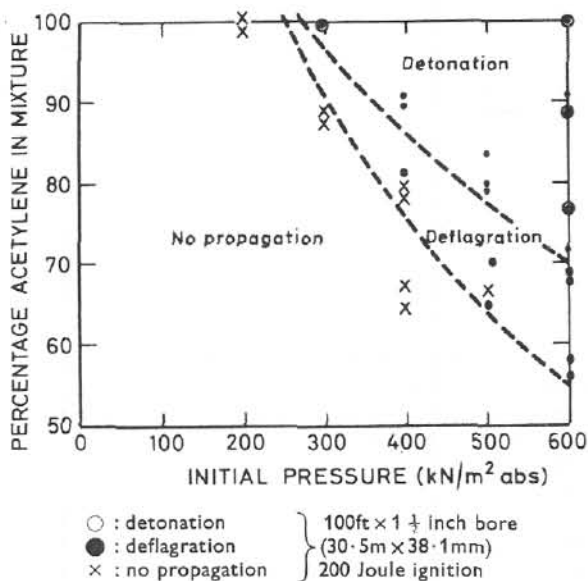

Fig. 2.—Acetylene. *Velocity of detonation as a function of tube diameter and pressure*

○ : ½ inch bore ⎫
△ : 1 inch bore ⎬ 200 Joule Ignition
□ : 1½ inch bore ⎭

● : ½ inch bore ⎫
▲ : 1 inch bore ⎬ gas ignition

○ : detonation ⎫ 100ft × 1 ½ inch bore
● : deflagration ⎬ (30·5m × 38·1mm)
× : no propagation ⎭ 200 Joule ignition

Fig. 4.—*Acetylene/nitrogen mixtures. Effect of pressure and dilution or limits of propagation*

○ : detonation ⎫ 100ft × 1 ½ inch bore
● : deflagration ⎬ (30·5m × 38·1mm)
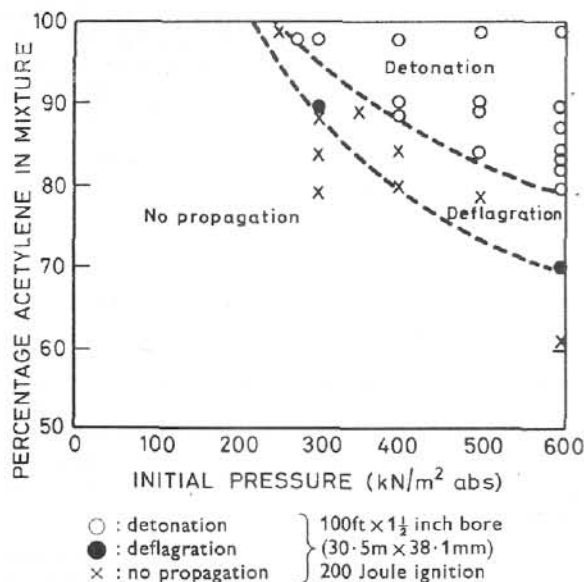× : no propagation ⎭ 200 Joule ignition

Fig. 6.—*Acetylene/carbon dioxide mixtures. Effect of pressure and dilution on limits of propagation*

obtained for ammonia were obtained, although the limits for both detonation and deflagration were at slightly higher *diluent concentrations*.

There seems to be little correlation between the physical properties of the gases and their ability to prevent decomposition. Overall, it appears that ammonia is slightly better than carbon dioxide, which in turn is significantly better than nitrogen. It seems, therefore, that the efficiency is probably dependent upon the chemical reactions that take place between the decomposing acetylene and the diluent. Unfortunately, very little gas analysis was carried out on the products formed in any of the reactions. The only information obtained was that in the case of carbon dioxide as diluent, the gases after the occurrence of a detonation no longer contained carbon dioxide. Hence it is not possible at this

stage to consider the efficiencies of the diluents from a consideration of energies of reaction.

In connection with problems associated with the separation of acetylene from the pyrolysis products of naphtha, the quenching effects of hydrogen, carbon monoxide, carbon dioxide, methane and ethylene on the propagating decomposition of acetylene, were examined at high pressure. The work was carried out in 30 m of 25 mm bore tube using 200 J exploding wire ignition. Results obtained at an initial pressure of $2 \cdot 76$ MN/m² abs. are given in Table I. The order of effectiveness of quenching was found to be methane, carbon dioxide, carbon monoxide, ethylene, and hydrogen.

TABLE I.—*Comparison of Various Diluents of Acetylene*

(25 mm × 30 m tube—200 J initiation)
Initial pressure ($2 \cdot 76$ MN/m² abs.)

	%C₂H₂			
Diluent	15	20	30	50
H_2	Did not propagate	Decomposed 186 s	Decomposed 61 s	Detonated
C_2H_4	—	Did not propagate	Decomposed 22 s	Detonated
CO	—	Did not propagate	Decomposed 110 s	Detonated
CH_4	—	—	Did not propagate	Decomposed 75 s
CO_2	—	—	Did not propagate	Decomposed 52 s

Times are for flame to travel 29 m

○ : detonation ⎫ 100ft × 1½ inch bore
● : deflagration ⎬ (30·5m × 38·1mm)
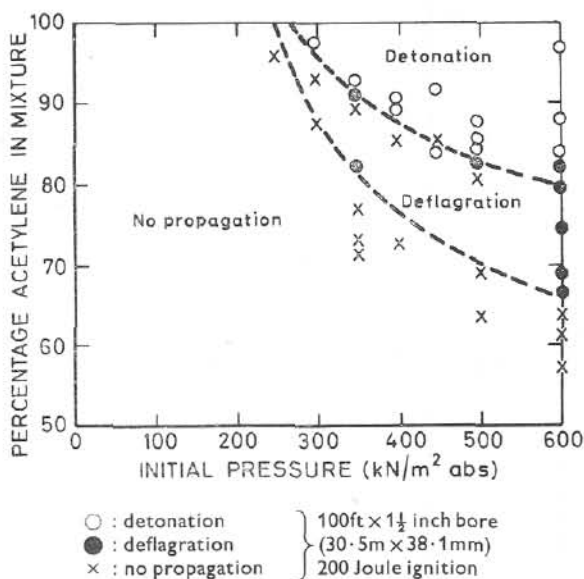× : no propagation ⎭ 200 Joule ignition

Fig. 5.—*Acetylene/Ammonia Mixtures. Effects of pressure and dilution on limits of propagation*

Decomposition of Acetylene in a 305 mm Diameter Pipeline

This work was associated with the transport of acetylene over long distances in large-bore pipelines; conditions that are used in many chemical plants.

A 61 m length of tube, 305 mm i.d. and 356 mm o.d. was assembled from 10 similar sections of seamless steel tubing.

Ionisation probes were fitted along its length at 3 m intervals. Velocity measurements were made by feeding time markers and the pulses from the probes into cathode ray oscillographs, which were photographed. The range of initial pressure of acetylene investigated was 25–200 kN/m² abs.

Three methods of initiation were used, namely:

(1). A tungsten wire coil, exploded by passing a nominal 200 J discharge through it.

(2). Ignition of an acetylene–oxygen mixture (70 : 30, v/v) in a 1 m length of tube at the same pressure as the acetylene in the main tube and separated from it by a 0·152 mm thick aluminium diaphragm. The particular ratio of gases was chosen because its detonation velocity is similar to that of pure acetylene, and it also avoids the possibility of surlpus oxygen entering the main firing tube which would effect the decomposition characteristics of the acetylene. An exploding tungsten wire was used to ignite the oxygen–acetylene mixture.

(3). Ignition of a 28 g pellet of 2, 4, 6, N-tetranitro-N-methylaniline with a No. 8 concave base aluminium sheathed detonator. The charge was mounted centrally in the tube, 152 mm from the end-plate, in a hardboard spider.

The results from the tungsten wire initiated experiments show some very interesting features, but at the present time, no definite conclusions have been drawn about them. There is a region of pressure between 100 and 200 kN/m² abs. where the velocity of decomposition builds up to supersonic level and in fact at 125 kN/m² abs., a detonation with a velocity of 2000 m/s was observed. However, at 200 kN/m² abs., although propagating decomposition occurred, the velocity failed to reach supersonic level, with respect to the unreacted gas.

Using oxygen–acetylene initiation, detonation velocities were set up between 75 and 100 kN/m² abs., but not at 50 kN/m² abs. At this latter pressure, the velocity of propagation decayed to approximately the speed of sound, a result similar to that obtained with a nitrogen-filled tube at 100 kN/m² abs.

With high explosive initiation, propagating detonations were established down to 50 kN/m² abs. At 25 kN/m² abs. the results show that an over-driven detonation started, but that the velocity was decaying rapidly and was approaching the speed of sound at the end of the tube. In fact, no decomposition occurred in the tube beyond the 30 m mark, as evidenced by the physical state of the probes.

The damage at the end of the tube in the tungsten wire initiated experiments, where detonation velocities were reached over the last few metres, was far greater than in those experiments where detonation was produced from the outset. This finding substantiates the view of Sargent[16, 17] that the greater the fraction of the tube covered by the deflagration before it transforms into a detonation, the greater will be the end pressure effect.

As expected, increasing the energy of initiation reduces the pressure at which acetylene can be induced to undergo self-propagating detonation.

Decomposition of Acetylene in a 12·7 mm Diameter Pipeline

The work was carried out in a 13·5 m length of cold-drawn steel tubing, 12·7 mm i.d. and 22 mm o.d., to simulate the conditions used in acetylene compressing stations. The tube was fitted with 15 bridge-wire flame detectors, and was closed by a bursting disc at one end and a firing plug at the other.

Three types of initiation system were used, namely:

(1). A 160 × 0·127 mm length of tungsten wire exploded by the discharge from a 100 μF capacitor bank charged to 2 kV (200 J).

(2). A 10 × 0·05 mm length of platinum wire exploded by the discharge from a 200 μF capacitor bank charged to 100 V (1 J).

(3). An acetylene/oxygen mixture (45 : 55, v/v) retained in the first 400 mm section of the firing tube by an aluminium diaphragm. This mixture was initiated by the 200 J tungsten wire system.

Velocity measurements were obtained by feeding time markers and the pulses from the probes into a cathode ray oscillograph which was photographed by a high speed drum camera. The resolution was 64 mm/ms.

The initial pressures investigated were between 200 and 3000 kN/m² abs.

A feature of all the experiments in which decomposition built up to detonation was the pronounced fluctuations in the velocities of the combustion waves. Even at the highest pressure used, 2860 kN/m² abs., the velocity fluctuated by a margin that was beyond the range of experimental error.

The lower pressure limit for detonation using the 200 J initiation was found to be between 466 and 487 kN/m² abs. With gas ignition, detonation occurred at the lowest line pressure used (i.e., 202 kN/m² abs.), and the velocity of propagation fluctuated markedly, indicating that the detonation was not being over-driven.

The average detonation velocities for both exploded wire and gas initiation are shown as a function of initial pressure in Fig. 7. As the initial pressure rises, the detonation velocity rises sharply and then levels out and approaches a limit of 1850 m/s at a pressure of 3000 kN/m² abs.

Another feature of all the experiments where detonation occurred was the magnitude of the terminal pressure. From classical detonation theory the ratio of the terminal to the initial pressure for an acetylene detonation should be 40 to 45 : 1. When discs with a bursting pressure of 60 or less times the initial pressure were used, they were removed cleanly and no visible traces of the material of the disc were found.

At high initial pressures, the main function of the bursting disc was to protect the end of the tube, hence, for example, at an initial pressure of 2·86 MN/m² abs., a disc with a burst-
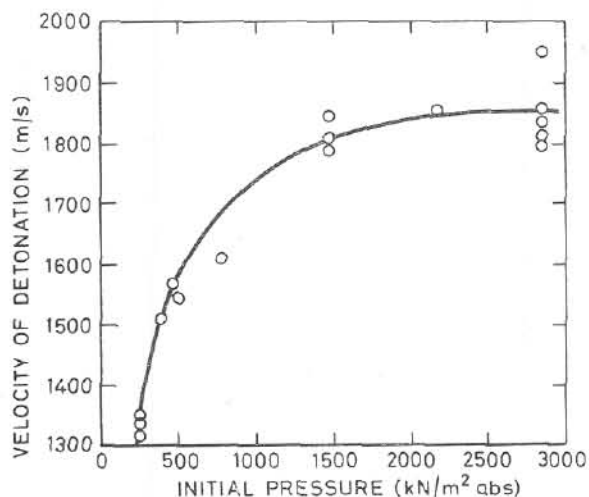

Fig. 7.—Acetylene. *Variation of mean velocity with pressure*

ing pressure of 181 MN/m² abs. was cleanly removed, showing that the pressure ratio was much greater than 63·1. At lower pressures, a much better idea of the magnitude of the terminal pressure was obtained. In one experiment with an initial pressure of 203 kN/m² abs., a bursting disc designed to relieve at 65 MN/m² abs. just failed; that is, the ratio was just greater than 320 : 1.

That the Sargent[16, 17] concept of pressure piling is not always applicable in cases where high terminal pressures are observed, is demonstrated by the experiment cited above where a pressure ratio greater than 320 : 1 was registered. In this case, initiation was induced by a shock wave from an oxygen–acetylene mixture and detonation was established in the acetylene within 1 m. It is felt that in such cases, the phenomenon of very high terminal pressures is due to the factors that give rise to the fluctuating velocities of detonation. Kogarko considers that in gaseous systems that are near the detonation limit, separation of the flame and shock fronts is a variable. When the separation is large in the vicinity of the end of a pipe, reflection of the shock wave from the end heats the unburnt gases prior to their detonation. Consequently, the pressures developed are much greater than would be expected from a consideration of the initial gas pressure.

Conclusions

The lower pressure limit for propagating detonation to occur in acetylene in pipelines depends markedly on the diameter of the pipe and the level of the initiation energy. The larger the diameter and the greater the energy of initiation, the lower is the pressure limit. This finding is in general agreement with the results of other workers in the field. Where the initiation energy is such that decomposition starts as a deflagration, there is a narrow range of initial pressures where the decomposition continues to propagate as a deflagration. Above this pressure range, the deflagration turns into a detonation provided that the pipeline is long enough. At high initial pressures, the run-up distance to detonation tends to a limiting value of 60 times the pipe diameter. Where the mode of initiation is such that detonation is established from the outset, propagating detonations occur at initial pressures lower than those required to support a propagating deflagration.

The terminal pressures developed in closed pipes are often very high in comparison to the pressures calculated from the classical detonation theory, an observation which has been made by several other workers. Although in experiments where there is a transition from deflagration to detonation, this effect can be explained by the Sargent concept of pressure piling, in those experiments where shock wave initiation produces a propagating detonation from the outset, an alternative explanation is necessary. The concept of an explosion within an explosion put forward by Oppenheim together with the idea of an unstable association of the shock and combustion fronts proposed by Kogarko, offer an explanation for this phenomenon.

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