

HAZARDS IN HANDLING ACETYLENE IN CHEMICAL PROCESSES PARTICULARLY UNDER PRESSURE

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SUMMARY

The explosive limits of acetylene in air are particularly wide—from 2.5 to 80%. All possible sources of ignition in the plant area must be eliminated, to avoid the risk of igniting flammable mixtures resulting from leaks in plant items. This includes the enclosure of any electrical equipment in the neighbourhood of the acetylene or to which leakage could penetrate, the housing being pressurised with air to a few inches water gauge. Decomposition of acetylene (on its own) liberates 54.1 kcal of heat per mole, and compressed acetylene can behave as a high explosive. Nevertheless commercial plants have been operated at pressures up to 20 atm. Possible sources of ignition within the acetylene-containing system must be avoided: these include silver and copper (or alloys of more than 70% copper), as decomposition of their acetylides can initiate explosions of the compressed acetylene.

Reactors should be heated by hot fluid rather than by electricity, and never by flame. Plant items need to be constructed so that if acetylene decomposition does occur within them detonation could not occur but the reaction should remain deflagration. Vessels should be designed for a test pressure of about 11 times the operating pressure, so that they will not burst when subjected to deflagration. Detonation can build up in long lengths of pipe lines and the pressure can rise by factors of 40-45 in the front of the explosion wave. Long lengths can be buried or laid in deep trenches and explosion arrestors be inserted where appropriate to prevent detonation passing into more sensitive items of equipment. With wide pipes, at pressures up to 30 lb/in²g, a tower filled with Raschig rings can be used to quench detonation. Reactions have been carried out experimentally without disaster at up to 150 atm when the reacting system was entirely a liquid phase, with no accompanying vapour, without using the 11-fold test-pressure factor.

Introduction

Acetylene has been available commercially for some sixty years, but for the first thirty years its main uses were for illumination and for the welding and cutting of metals; the only large-scale use in chemical synthesis before 1925 was the preparation of acetaldehyde which was developed during the first world war. The use of acetylene as a fuel gas is still increasing, but now there is a much greater and more rapidly rising demand for acetylene for a variety of large scale chemical syntheses which have been developed in the last two or three decades.

Most of the acetylene used in these processes is at about atmospheric pressure or only up to about 1 atm g. In addition to the manufacture of acetaldehyde already mentioned, the syntheses for which acetylene is required include vinyl chloride, vinyl acetate, other vinyl esters, acrylonitrile, acetylene black, trichloroethylene, vinylacetylene (for neoprene), etc. There are hazards when working with acetylene even at pressures such as 1 atm g, but much more serious additional hazards arise when working with acetylene at higher pressures. In Germany during the early part of the war large-scale processes were operated requiring the use of acetylene under pressure and the explosion hazards were kept under control. The largest of these processes was the production of butynediol, and a plant of capacity 30 000 tons per annum was operated at Ludwigshafen by I.G. Farben. The product was used as an intermediate in the manufacture of Buna rubber. Other processes using acetylene under pressure include the manufacture of polyvinylpyrrolidone, of some

vinyl ethers, and of acrylic esters. Some of this work was taken up in America after the war, and to a smaller extent in other parts of the world.

Nature of the Hazards

Flammation

The main hazard in dealing with acetylene at normal pressure—a hazard which, of course, is present with compressed acetylene—is that which is common to all flammable gases. This is the danger of explosive flammation, either within the plant through adventitious ingress of air, or externally, following leakage of the flammable gas. This danger is, however, particularly acute with acetylene, because it has such wide explosive limits when mixed with air, *viz.* 2.5-80%. Explosion could follow leakage into a fairly confined space, being initiated by a flame or by a spark from electrical equipment; as yet no electric motors or switchgear have been certified as "flameproof" for use in acetylene-containing atmospheres.

Initiation of explosive acetylene decomposition

The other hazards with compressed acetylene arise from its ability to decompose exothermally under certain conditions in complete absence of oxidising or other reactants. It is thermodynamically unstable in respect of its elements at room temperature, and the overall reaction $C_2H_2 = 2C + H_2$ liberates 54.1 kcal per mole.

All the recorded ways of initiating the explosion of acetylene under pressure involve the production of a point of local heating. The decomposition temperature of acetylene at 2 atm abs has been stated to be 510°C.¹ The present authors

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have measured the temperature at which acetylene at 3–25 atm g becomes subject to explosive decomposition, by admitting acetylene into a heated steel tube which had previously been evacuated. The explosion temperature is independent of pressure over the range studied, but it is reduced considerably by the presence of small amounts of finely powdered materials. The results in Table I were obtained with 1 gram of such powders at the centre of a pipe 15 in. long and $\frac{1}{2}$ in. diameter; and the powdered materials examined included rust, pipe-scale, kieselguhr, alumina, silica gel, and charcoal.

TABLE I.—Temperature needed to Initiate Explosion of Acetylene in Steel Pipe at 3–25 atm

Clean empty tube	400–425° C
In presence of 1g of powder	280–300° C
In presence of 1g of solid potassium hydroxide ..	170° C

The authors believe that exothermic condensation reactions occur on the surface of the solid material which raise its temperature to the 450°C needed to initiate gas phase decomposition.

It is well known that certain acetylides, particularly copper and silver, are themselves capable of explosive decomposition. The explosion of copper acetylide is rarely in itself a hazard because the quantities of this material normally isolated and handled or obtained adventitiously in the use of acetylene are small. The intrinsic hazard of copper acetylide is the capacity of certain varieties to decompose upon extremely mild initiation, and thereby produce hot spots sufficient to set off acetylene decomposition.

This was illustrated by preparing a particularly sensitive variety of copper acetylide, as a black flaky material, by bubbling acetylene through slightly acidic solutions of cupric salts,² and drying the precipitate. A fragment was placed on an anvil inside a tube, to which acetylene was later admitted at a pressure of 3 atm.

A $\frac{1}{4}$ in. steel ball was magnetically held 15 in. above the anvil within the tube, and then allowed to drop. This was sufficient to decompose the copper acetylide, which in turn

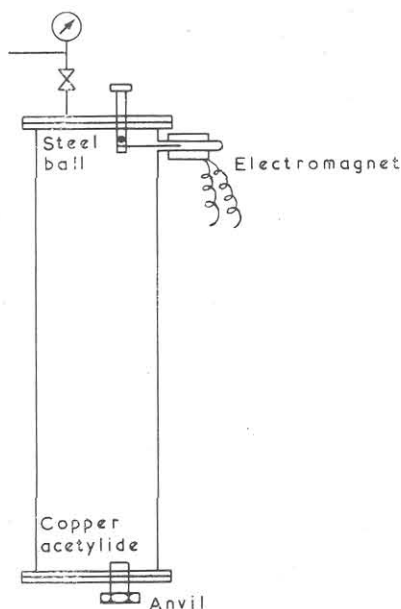


Fig. 1.—Ignition of acetylene by impact of copper acetylide

set up an explosive decomposition in the gaseous acetylene. The apparatus is indicated in Fig. 1.

Copper acetylide can also be formed from metallic copper by prolonged exposure to acetylene, particularly if the surface of the copper has previously been corroded. The nature of the film is dependent on the copper content of the alloy. If this is low (less than 65–70%) the acetylide film (if formed at all) remains extremely thin and adherent to the metal; such films cannot be made to spark by friction or by contact with a wire heated to 150°C. Copper acetylide films on alloys of higher copper contents or on pure copper can become thicker, and it may be possible to flake them off the surface of the metal. If detached from the metal, this acetylide is still not as sensitive as that formed by wet methods from copper salts, and cannot be ignited by the steel-ball test described, but it is still sufficiently sensitive to be ignited by friction or by hot wire at 150°C.

Explosive complex mercury acetylides can be formed by passing acetylene through solutions of mercuric salts under particular conditions. Mercury acetylides cannot however be formed directly from metallic mercury and acetylene, even in presence of dilute acids.

Silver acetylide is readily formed when acetylene is passed through silver nitrate solution. It is intrinsically a much more powerful explosive than even the most sensitive copper acetylide. Equal amounts of silver and copper acetylides were placed in test tubes behind Perspex screens; the acetylides were then exploded by electrically fusing a wire embedded in them. The copper acetylide decomposition was contained within the glass test tube, but the exploding silver acetylide shattered the tube and also fragmented the Perspex screen. Detailed study of the type of acetylide formed directly from silver and acetylene is not available, but the authors have observed explosive deposits on silver solder exposed to acetylene.

Nickel does not form an acetylide.

A possible source of point-heating in acetylene could be the frictional hot spots produced on opening a valve, especially if a fragment of grit has become lodged in the seating. In the ordinary use of acetylene in industry, valves are opened millions of times annually to allow passage of compressed acetylene from cylinders, manifolds, compressors, etc. Perhaps one in a hundred million of such valve openings has been followed by a sequence of events finally resulting in an explosive acetylene decomposition, but there have been so few that it has not been possible to discover whether the primary initiation of the explosion was friction within the valve or some highly adventitious accompanying cause. In the authors' own experimental work, initiation of this type was experienced only once, and this was when using a cock in which a stainless steel spindle rotated within a non-metallic sleeve (and frictional hotspots would be therefore least expected). Acetylene was being passed at a pressure of 18 atm into a closed pipe, $2\frac{1}{2}$ ft \times $\frac{3}{4}$ in. containing air at atmospheric pressure. There was a piece of platinum wire, 1 cm long, at the far end of the pipe. The explosion started when the cock was one-third open, but the mechanism of initiation could not be elucidated.

In spite of the field experience, it was suggested some years ago³ that valves with metal-to-metal seatings were capable of initiating acetylene explosions. The authors attempted to investigate this experimentally. A test valve was placed between two vessels, each 3 ft \times 3 in., and the valve was opened and shut mechanically. The apparatus is shown in Fig. 2.

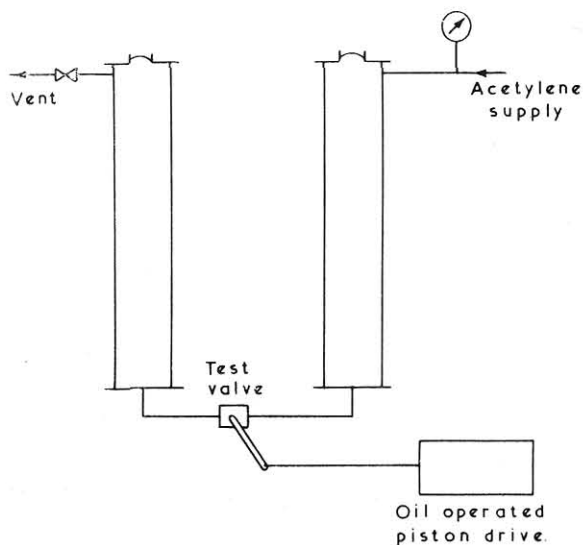


Fig. 2.—Automatic valve-tester

The first vessel was connected to an acetylene compressor so as to maintain its pressure at 20 atm. The second vessel had another valve which was kept slightly open, so that acetylene flowed through the whole system each time the test valve was opened. The test valve was opened and shut 10 000 times, and no decomposition was initiated in the acetylene.

In order to see whether this negative result applied only to a clean valve, a little concrete dust and iron rust was put into the seating of the valve, and the experiment was repeated for another 10 000 operations. No explosion was initiated. In a further experiment, the foreign material introduced into the valve seating was a mixture of charcoal and copper acetylide, and here again no explosion could be initiated by 10 000 operations of the valve.

Deflagration

The 54.1 k cal of heat liberated in the decomposition of a mole of acetylene would be sufficient to raise the temperature of the resulting carbon and hydrogen to 3100°C if there were no heat loss. At this temperature, however, there would be an equilibrium concentration of about 6% of acetylene. The authors have analysed the residual gas after the experimental explosive decomposition of acetylene (initially at 3.4 atm abs) in a long pipe, and found that it contained no acetylene, but consisted of 92.2% hydrogen, 5.5% methane, and 2.3% olefines (mainly, and possibly entirely, ethylene). It is thought that there may nevertheless have been acetylene in the explosion wave front, and that the methane and ethylene were formed from it, in presence of the hydrogen, during the cooling down after the explosion wave had passed. If allowance is made for the undecomposed acetylene in equilibrium at the high temperature, and also for heat absorbed in some dissociation of hydrogen molecules into atoms, it can be shown that the temperature reached on decomposition (assuming no heat loss by radiation, etc.) would be between 2800 and 2900°C, depending somewhat on the initial pressure of the acetylene (since the dissociation equilibrium of hydrogen molecules is pressure dependent). This temperature would give a rise in pressure by a factor of $10\frac{1}{2}$ –11.

Rimarski⁴ records the explosion of acetylene initially at 1.40 atm abs in a vessel of 27 cm diameter; his final pressure was 13 atm abs, a rise by a factor of 9.3. The authors have carried out several determinations of pressure rise in a vessel 12 in. × 2 in., initiating acetylene decomposition by the fusion of a platinum wire 1 cm long × 0.2 mm. In 16 experiments with an initial pressure of 9.0 atm abs the average final pressure was 100.2 atm abs (with a standard deviation of only 5.3 atm). This pressure rise of 11.1 times agrees very well with the calculated factor given above.

The time taken for the pressure rise to occur was also measured; the time between initiation and the onset of pressure rise was variable, being anything from 3 to 45 ms, but the pressure rise itself always occurred in 3 ms or less, as shown by Fig. 3.

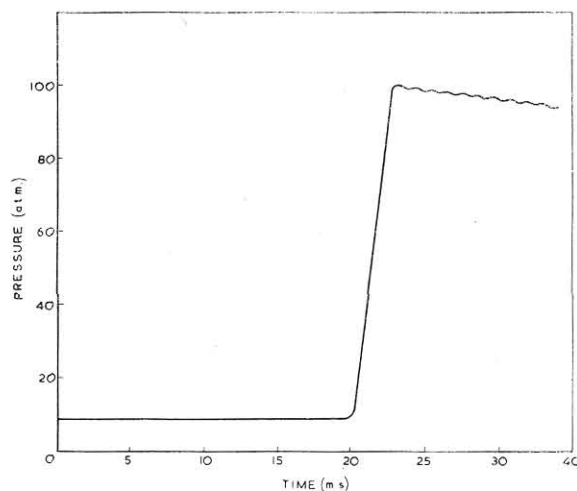


Fig. 3.—Pressure-time record for deflagrative explosion of acetylene

The experiments had been designed to determine the velocity of deflagration, but, as stated, the time measured over the (fixed) distance between the fused wire and the pressure gauge was unreproducible, and the velocities measured ranged from 10–100 m/s.

It had long been believed that there was a minimum pressure of 1.4 atm abs (5.9 lb/in²) below which self-propagating explosions could not be induced in acetylene.

The critical minimum pressure had been related to the diameter of the pipe, decreasing with increase in diameter to the above value for the widest pipes⁵ as indicated by Fig. 4.

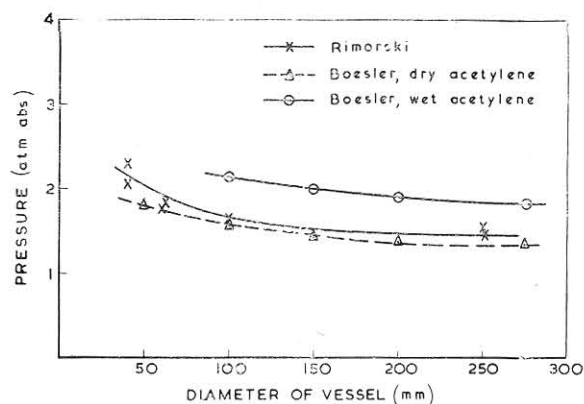


Fig. 4.—Limiting pressure for decomposition of wet and dry acetylene as a function of vessel diameter

It was therefore considered that acetylene could safely be piped over indefinite distances if the pressure was not much above ambient, say that of a gasholder (12 in. water gauge = 1.03 atm abs). On 2 January, 1954, however, a serious explosion occurred at Chemische Werke Hüls, involving over a mile of pipeline of 6 in. and 12 in. diameter, and attached equipment. In a subsequent study,⁶ it was confirmed that progressive decomposition of acetylene could be set up in 12 in. diameter pipe at gasholder pressure, and even at slightly sub-atmospheric pressures, if the initiation occurred across the whole cross-section of the pipe at the same time. This was achieved by using a forechamber with acetylene at a higher pressure (2.5 atm abs), causing the acetylene in the forechamber to decompose by the fusion of a wire, and communicating the explosion to the gas at lower pressure by the bursting of a bursting disc which separated the forechamber from the main experimental pipe. Direct initiation of the lower-pressure gas by the fusion of a platinum wire would not set up a progressive decomposition. Analysis of the conditions of the incident of 1954 suggested that initiation across the whole pipe had indeed occurred by a sequence of mishaps which resulted in the admission of compressed chlorine into the acetylene line.

Detonation

As it travels over increasing distances, the deflagrative decomposition wave accelerates to velocities of some hundreds of metres per second, and the explosion then rapidly passes into detonation, whereby the velocity of propagation rises severalfold; the pressure developed rises to 20–25 times the initial pressure for a period of many milliseconds (the "Chapman-Jouget plane"), and indeed to 40–45 times for a few microseconds (the "van Neumann peak"). Relationships between onset of detonation and length of pipe, diameter and initial pressure of gas have not been worked out in detail for acetylene, neither alone nor in presence of diluents.

The pressure ratios quoted above have been calculated⁷ from classical detonation theory,⁸ but the present authors' attempts to measure the pressure rise directly gave inconsistent results. The same calculations⁷ led to a velocity of detonation of 2053 m/s for acetylene at an initial pressure of 8 atm abs.

The velocity was then measured in pipes of 1 in. and $\frac{1}{2}$ in. diameter using the circuit shown in Fig. 5. Fig. 6 shows a typical trace obtained on the double beam oscilloscope. In

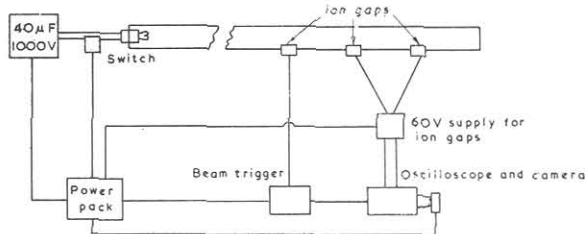


Fig. 5.—Explosion velocity measurement



Fig. 6.—An oscilloscope record

the 1 in. pipe the velocity was 1870 m/s (with standard deviation 22), and in the $\frac{1}{2}$ in. pipe the velocity was 1817 m/s (standard deviation 7). When these results are plotted against the reciprocal of the diameter of the pipe, as in Fig. 7, extrapolation gives a value of 1923 m/s for the limiting detonation velocity in pipe of infinite diameter. The agreement with theory is close enough to show that acetylene behaves like a conventional high explosive, and therefore that the detonation pressures calculated from theory are also of the right order. The discrepancy in velocity between experiment and calculation must arise from incomplete knowledge of the true composition of the detonation wave front; the heat release is slightly less in fact than the amount used in the calculation, possibly because the carbon retains "surface energy",⁹ or contains a slight amount of combined hydrogen, or possibly because some of the carbon is gaseous, *i.e.* its vapour pressure is above that of the equilibrium vapour pressure of solid carbon at the explosion temperature. Enhancement of vapour pressure in gases at high pressure has been observed in several systems.

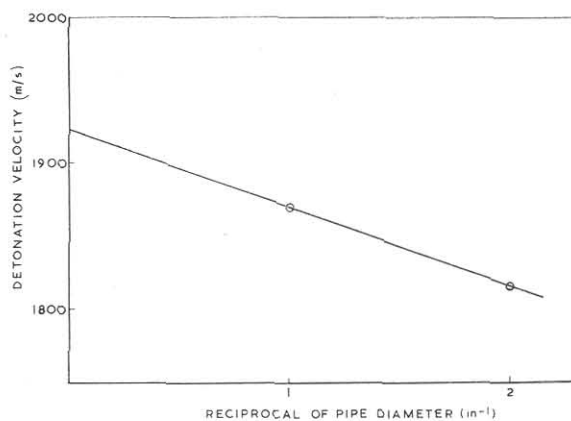


Fig. 7.—Detonation velocity of acetylene in $\frac{1}{2}$ in. and 1 in. pipes at pressure of 8 atm abs

Measures Against the Hazards

External flammation

Hazards arising from the ready flammability of acetylene in air demand, in the first place, a high standard of plant construction and maintenance to obviate the possibilities of flammable mixtures being obtained either by ingress of air into plant items or by leakage of acetylene. The plant area should be adequately ventilated, so that even if leakage does occur, the flammable range should not be reached. Even if flammable mixtures should nevertheless transpire in the plant area, the possibility of their being subjected to sources of ignition should be removed. Obviously naked flames must be excluded, but in addition electric starters, switchgear, and motors should be housed in separate rooms or enclosures away from the plant.

In the authors' work on the use of acetylene for chemical processing, all the electrical equipment, including lights and wiring, was enclosed and the enclosures and conduit were pressurised with dry air to a pressure of a few inches water gauge. This ensures that any leakage of flammable material would not come into contact with potential sources of electrical ignition.

Sources of internal initiation

Since acetylene can be initiated by a surface at 425°C or by powdered material at 280°C, vessels should not be heated by direct flame, and preferably by hot fluids rather than directly by electricity.

Copper and high-copper alloys need to be avoided for vessels and pipes containing pressurised acetylene; even low-copper alloys are best avoided for substantial items of plant, especially where there is any possibility of corrosion by acidic agents. Brass or bronze fittings external to the plant do not present much hazard. They can (and should) be kept clean by good housekeeping, and appreciable deposits of acetylide should not be allowed to build up. Even if they did, the copper acetylide deposit on the brass or bronze is not sensitive, and is not in places where it could set off an explosion in pressurised acetylene. Even small amounts of silver in any form need to be excluded from plant using compressed acetylene.

The use of mercury in instruments attached to acetylene-using plant does not in itself appear to produce a source of hazard. Nickel and nickel alloys can be used freely where needed. There seems to be no case for preferring any particular type of valve from safety considerations alone.

Vessels

In spite of all precautions to avoid sources of initiation, it has to be accepted that initiation of explosion may nevertheless occur, and reactors, etc., need to be strong enough not to burst even when such an explosion occurs. In order not to impose an unnecessarily heavy design factor the vessels need only be such as to withstand deflagration but not detonation pressures: measures to ensure that detonation cannot take place within them will be discussed later.

The pressure-rise in deflagration is about 11-fold, so that vessels built to a test pressure (not a working pressure) of 11 times the working pressure are needed.

Some work has been carried out to see whether this safety margin could be reduced by incorporating appropriate bursting discs in a vessel. A test vessel 15 in. \times 4½ in. was fitted at one end with a bursting disc of 2 in. diameter set to operate at 32–33 atm. Explosions in the acetylene in the vessel were initiated by the fusion of platinum wires at various distances from the bursting disc, and also by passage of an explosion into the vessel through a ½ in. diameter pipe attached to the midpoint of the vessel wall. The explosion pressures were measured by condenser gauges at various points within the vessel.

TABLE II.—Some Explosion Pressures in a Vessel with a Bursting Disc to fail at 32 atm

	(atm)	(atm)
Initial acetylene pressure	10	20
Pressure near bursting disc:		
Explosion initiated at furthest point	50	136
Explosion led in by attached pipe	70	150

Thus even a bursting disc relatively large compared with the diameter of the vessel cannot prevent pressures much larger than the operating pressure of the disc being experienced, although it does somewhat reduce the full 11-fold rise in pressure which would otherwise be attained. The protective value of bursting discs for this purpose is therefore limited.

Bursting discs may however be valuable in reactors with gas and liquid phases, as reactions between acetylene and other reactants in the liquid phase may accelerate without becoming explosive; a bursting disc would effectively limit

the rise in pressure consequent on acetylene (and other solutes) being forced out of solution by the heat liberated, and therefore may prevent a gas-phase explosion which might otherwise ultimately occur.

Reaction vessels need to be of such dimensions that deflagrations initiated within them cannot pass into detonations. This is a function of the length to diameter ratio of the maximum gas space which might be present in various stages of use, and of the working pressure. Work in pipes of ½ in.–12 in. diameter suggests that the length to diameter ratio for detonation to build up drops from about 200:1 at 15 lb/in²g to 10:1 at over 200 lb/in²g.¹⁰ No measurements are available at 300 lb/in²g. It seems that an adequate margin of safety would be maintained if acetylene gas phases under high pressure in reactors were limited to regions of not more than 3 ft long and 1 ft diameter. If the scale of operation demanded larger gas spaces than this, considerable further study of the build-up of detonation would be needed.

Considerable importance has been attached in reports of the German plants using acetylene at pressures higher than 5.5 atm abs to the use of diluents, particularly nitrogen. For example, in the German vinyl ether process¹¹ operating at 18–22 atm the proportion of nitrogen in the recycle gas was 55%, and after injection of fresh acetylene, the gas fed into the reaction vessel contained 45% nitrogen. Experimental work in Germany^{5, 12} had however previously shown that the proportion of nitrogen needed to make a mixture non-explosive at 20 atm was 65% at 15°C and 70% at 100°C. The results of tests in a tube 1m long \times 9 cm with acetylene-nitrogen mixtures at up to 200 atm are shown in Fig. 8. The present authors, working with a 1 in. pipe, found that a mixture containing 48% of nitrogen would sustain progressive explosion even at a total pressure of only 7 atm.

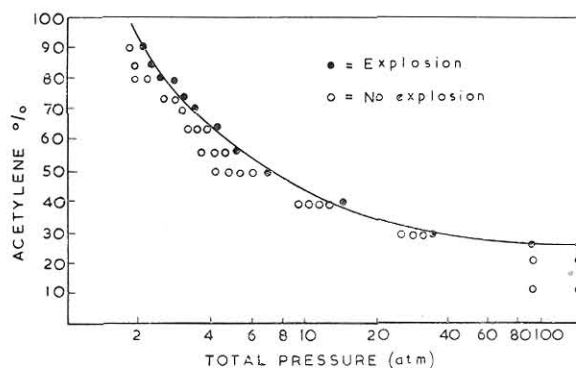


Fig. 8.—Limiting pressure for explosive decomposition of acetylene nitrogen mixtures

In general, the extent of dilution needed to suppress completely the hazard of explosive decomposition of acetylene is such that it would be intolerable in manufacturing processes, as it would effectively reduce the partial pressure of acetylene for reaction purposes. There may be a region of dilution in which explosions are more easily confined to deflagration rather than detonation, but these regions have not been delimited. The authors' evidence, as far as it goes, suggests that detonation still remains possible if the length to diameter ratio is high enough, even at appreciable dilution. The hazards which have to be faced and allowed for are not appreciably reduced by the introduction of diluents in reasonable amounts.

Explosion arrestors

It has been seen that it is advisable to build reactors and other vessels to withstand deflagration explosion without bursting, and to limit their size so that detonation cannot develop within them. It is essential to ensure that detonation cannot be passed into such vessels from pipe lines attached to them.

The problem of superimposed detonation can arise either from wide pipes carrying acetylene at comparatively low pressures over long distances, or from narrower pipes carrying the compressed acetylene from stage to stage within the high pressure plant.

As has been shown, pipes of 12 in. diameter can sustain acetylene explosion even at atmospheric pressure. Even if the acetylene is to be used at or about this pressure, it is often desirable from considerations of the operation of the plant to convey it at pressures of perhaps 15 or 22 lb/in²g (which are commonly used for this purpose). At such pressures, pipelines of less than 12 in. diameter also introduce the possibility of adventitious explosion of acetylene in the pipeline, and if the line is long enough, such decomposition may progress into detonation. If Class C seamless pipes are used, the pipe itself is usually strong enough not to rupture even when detonation occurs, but in some installations it has been deemed advisable to bury as much of the pipe as possible, or to introduce some other means of protecting personnel. Equipment at each end of the plant might however include items built to withstand deflagration but not detonation, such as compressors or reactors, or items which cannot be reasonably built to withstand even deflagration and in which deflagration is extremely unlikely to be initiated in the items themselves, such as gasholders, gas meters or purification systems. To counter the hazard of communicated explosion, installations have been designed for use at the end of long pipelines to quench an explosion wave, whether it is deflagrative or detonative in character.

One such type of explosion arrestor was tested by Schmidt and Haberl⁶ and is in use in America and Britain. Essentially it comprises a tower packed with Raschig rings which are irrigated with water. The authors have tested such a tower, 10 in. diameter packed with 1 in. Raschig rings to a depth of 4 ft and attached to 600 ft of 3 in. diameter line containing acetylene at 30 lb/in²g (3 atm abs). The apparatus is shown in Fig. 9.

Initiation of the explosion was effected across the whole diameter of the pipe by attaching to the end of the pipe furthest from the tower a 3 ft length of pipe separated from the main run of pipe by a bursting disc. The pipe contained acetylene at 8 atm abs. The acetylene in the forechamber was exploded by the fusion of a platinum wire 1 cm × 0.2 mm, using a 24v battery. The velocity of the explosion wave before it entered the tower was 1750 m/s, which confirmed that detonation was set up.

Pressure measurements were attempted, using condenser gauges at various points in the tower, but the records were confused by oscillations caused by vibrations induced in the steel of the tower walls. Thermocouples showed that there was no rise in temperature 1 ft above the point of entry of the explosion into the tower. Indeed, the evidence from visual examination showed that the explosion had been completely quenched in the first few inches of the tower. The system as tested was, however, completely closed, and even though the explosion was quenched, bursting discs set to operate at 10 atm functioned either at the top of the tower or at the end of the 20 ft run of outlet pipe from the tower. A consider-

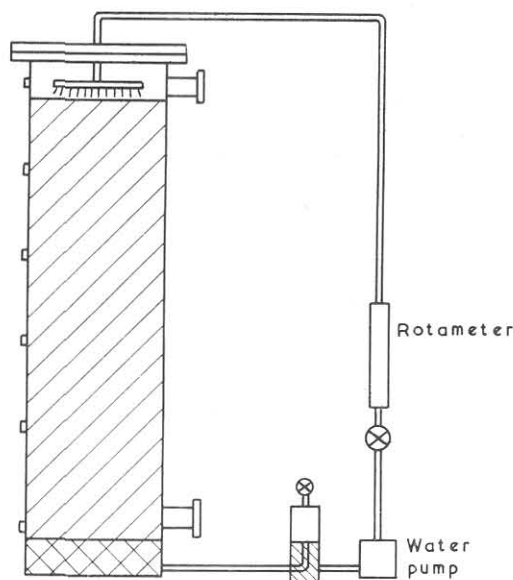


Fig. 9.—Water-irrigated packed-tower explosion arrestor

able amount of gas in the pipe had been heated to some 2800°C and raised to a pressure of about 70 atm; this gas did not instantaneously revert to atmospheric temperature and pressure after the passage of the explosion wave so that a pressure-pulse in excess of 10 atm passed into the gas beyond the tower, into gas in which no explosion had occurred.

This pulse would be undesirable in practice, so a bursting disc functioning at 10 atm was inserted on a T-junction near the point of entry to the tower. The outlet from this disc was arranged vertically upwards. When the acetylene in the pipeline was exploded, the functioning of this disc provided an escape for gas and the pressure-pulse passing through the tower after the quenching of the explosion was limited to about 50 lb/in²g, *i.e.* less than twice the original pressure.

Further work showed that complete quenching of the explosion (and limitation of the pressure-pulse) could be achieved even with dry Raschig rings in the tower, except that under such conditions the explosion was only completely quenched after it had traversed 1–1½ ft of the rings, as compared with only a few inches of the irrigated rings.

When acetylene is carried at higher pressures than 30 lb/in² the runs of pipe are likely to be smaller in diameter: at such pressures detonation can be set up in these narrower pipes and in much shorter runs. In the German butynediol plant, which operated at 5.5 atm abs, but not the plants operating at 20 atm, the packing of pipes with bundles of narrow tubes is featured.¹³ Their purpose was to prevent deflagrations building up into detonations, since the reactors etc. into which the pipes led were designed to withstand deflagrations but not detonations.

Experiments at Griesheim⁵ around 1940 suggested that such tube bundles in pipes of up to 6 in. diameter could prevent detonation if the initial pressure was not above 4 atm, but they served no useful purpose at initial pressures of 8 atm g. The present authors have confirmed the uselessness of narrow tubes at pressures above 9 atm g, because they find that at all pressures above this, detonation is set up and travels through tubes as narrow as ⅓ in. diameter.

Some data on the length of pipe needed for detonation to occur have been obtained using 100 ft runs of 1 in. pipe, by

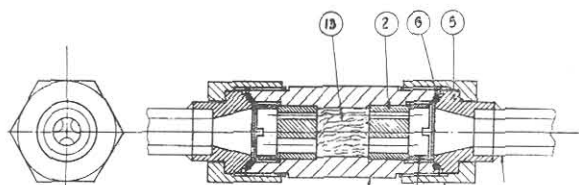


Fig. 10.—Steel wool explosion arrester assembly

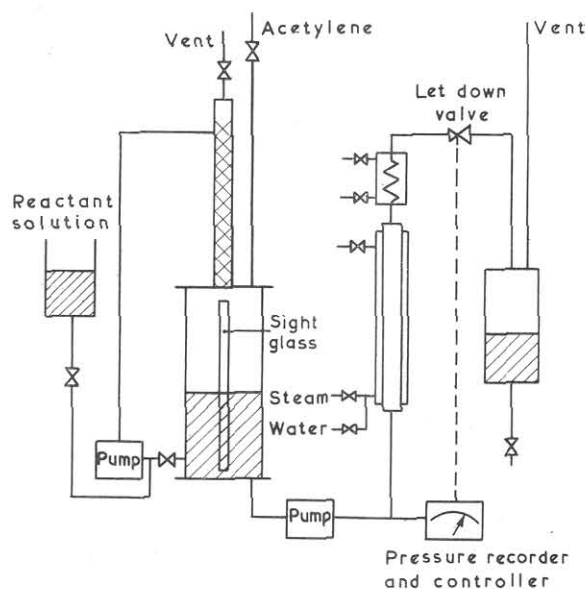


Fig. 11.—Experimental plant for acetylene reactions at high pressure (120 atm) in single, liquid phase

initiating explosion by fusing a platinum wire at one end. At pressures below $3\frac{1}{2}$ atm abs the decomposition wave tends to die out in about 12 ft, but at all higher pressures detonation developed. The distance needed for the detonation to develop decreases markedly with rise in initial pressure. The results are given in Table III.

Initial pressure (atm abs)	3.5	3.8	5.0	20.0
Length for detonation (ft)	30	22	12	2.8–3.2

It was found that bursting discs in the pipeline operated, but they do not prevent the build-up of detonation nor do they arrest or damp down detonation once it is set up.

In order to prevent detonation in a pipe (which is likely to be able to withstand it without bursting) causing detonation in attached items of plant (which have been designed to resist bursting in deflagration only) it is necessary to insert explosion arrestors between pipelines and vessels.

There have been many designs of arrestors for acetylene decompositions, mainly for use in acetylene compressing stations when filling cylinders. The explosion arrester for acetylene decomposition is based on the usual general principle of flame arrestors, *viz.* the presentation to the path of the explosion of a large surface to remove the heat quickly

from the flame front. In the case of acetylene, very fine passages have to be used in the arrester. It has been proposed to do this by various forms of plugs of compressed powders, but many of these, whilst effective in suppressing detonation, offer very considerable resistance to the normal flow of gas.

One satisfactory form of arrester consists essentially of sintered metal hollow cylinders,¹⁴ the gas flowing first into an annular space between the cylinders and an outer pipe, then through the cylinder walls. The cylinders need to be supported from the inside to prevent them being crushed by the force of the explosion wave; also they cannot always tolerate an explosion wave passing within them outwards, and therefore the arrester has to be so constructed that an explosion coming from either direction first meets the outer surface of the sintered metal cylinders.

Other flash arrestors have been constructed from shredded metal such as steel wool. In the Reichanstalt,⁵ compressed steel wool sponges were found to arrest detonations in 5 in. diameter pipe at pressures up to 6 atm. Later work at Griesheim found that in 8 in. pipe, detonations were arrested by compressed steel wool, but on occasions the explosion was re-initiated after some considerable time (up to 20 minutes), a slow flame eating its way through the steel wool packing in this period.

The authors have studied the arresting of detonation at higher pressures in a narrower pipe. Under these conditions, steel wool plugs 1 in. long compressed to a porosity of 75% have been found to be always effective in suppressing detonation. Difficulties arose through damage to the retaining perforated plates under the impact of the detonation, and such difficulties could be overcome by various mechanical devices; one such involves an arrester of outer diameter somewhat larger than the pipeline with a conical element in the expansion junction.⁵ This attenuates the explosion wave sufficiently to avoid damaging the retention plates.

A typical assembly is shown in Fig. 10.

Very High Pressure Work

The chemical reactions for which compressed acetylene has been used or proposed are all liquid-phase, and the acetylene is compressed in order to maintain a sufficiently high concentration in the liquid for reasonable rates of reaction. Whereas liquid acetylene, especially if compressed, has been known to explode very violently, explosions in systems containing acetylene and solvents appear to occur exclusively in the gaseous phase. The reaction between acetylene and a solvent or another reactant in solution in the same solvent may accelerate very rapidly under certain conditions, but explosive conditions have not been recorded. The consequences of acceleration of reactions should be controllable by bursting discs or relief valves in conventional manner.

It has therefore been considered that if acetylene is reacted in a system in which there is only a liquid phase, much higher pressures can be tolerated.^{16, 17, 18, 19}

In principle the system used is to dissolve acetylene with the other reactants in the solvent at ambient or sub-ambient temperatures, and then to pump the solution into a reactor which is maintained at the necessary temperature for reaction and in which the pressure rises to a value greater than that needed to maintain the acetylene in solution at the reaction temperature. The reacted liquid then flows through a reducing valve, so that there is no gas phase at all at the high pressure in the reactor. Fig. 11 shows the plant used.

It is not yet known whether any actual production units have been based on this principle. It has however been

applied on an experimental basis to the production of vinyl ethers from acetylene and alcohols with alkaline catalysts, to the production of *cyclo*-octatetraene from acetylene itself in solution in the appropriate solvent in presence of nickel catalysts, to the vinylation of pyrrolidine, etc. The authors have studied these reactions at up to 150 atm, the reducing valve in the reactor being set to allow reacted liquid to pass out when this pressure is reached. Explosions have never been experienced in this liquid-phase reactor, although uncontrollable slow rises in pressure have occurred which have been completely relieved by the functioning of bursting disc rated to operate at 200 atm.

Conclusions

In handling acetylene for chemical reactions carried out under pressure, the following precautions need to be taken:—

All possible sources of ignition of an acetylene-air mixture external to the plant items must be avoided. Electrical equipment should be housed as far as possible in rooms separate from places where acetylene is being handled, and any electrical equipment still remaining in places to which leakage of acetylene can penetrate should be totally enclosed, and the housing enclosing it (including conduit carrying electrical leads) should be pressurised to a few inches of water gauge with dry air.

Potential sources of ignition within the acetylene-containing system must be avoided. Reactors should never be heated by flame and, preferably, not directly by electricity, but by hot fluids. Silver in any form must be avoided, and so must copper or copper alloys containing more than 70% of copper. Even alloys of lower copper content could well be avoided where equally satisfactory alternatives exist.

Reactors and other plant items containing acetylene under pressure should be so designed that at no time is the length of the gas phase more than four times its diameter, and the item should have a test pressure 11 times the operating pressure. A suitable explosion arrestor needs to be inserted in the pipe leading into or out of the vessel, near the point of entry. As an ultimate precaution, to protect personnel against injury should all the above safety measures fail, reactors and other dangerous plant items should be installed in the open or in rooms whose roofs include a light blow-off cover, and the operators should work with an appropriate wall between them and the compressed-acetylene vessels. Instrumentation needs to be arranged accordingly.

Long runs of wide pipeline carrying acetylene at medium pressures should be buried or laid in deep trenches, and explosion arrestors be interposed between the pipeline and the equipment for feeding acetylene into it, and also for taking acetylene from it. One type of arrestor comprises a tower filled with Raschig rings.

Reactors designed and operated so as to contain the acetylene only in solution, with no gas-phase at any time, can be protected with bursting discs, without requiring the 11-fold test factor.

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