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SOME ASPECTS OF UNCONFINED GAS AND VAPOUR CLOUD EXPLOSIONS

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Summary

The experimental and theoretical work on the various phenomena normally considered under the heading of unconfined explosions has been critically assessed. Special attention has been paid to studies which may provide models of phenomena involved.

Introduction

Until recently there was relatively little written on the subject of unconfined gas and vapour cloud explosions. In addition much of the work was issued in the form of limited circulation reports rather than in the open literature. This situation has changed recently and there has been a major growth of research into this area. This expansion of work is almost certainly due to incidents such as those at Flixborough in the U.K. [1,2] and Beek [3] in Holland and represents what is likely to be a developing trend in the future.

At present there exist three major surveys of work in this field. The first is due to Strehlow [4] and is primarily concerned with collating data from actual incidents, although a certain amount of theoretical and experimental work is discussed. The second is due to Strehlow and Baker [5]. This report covers an extremely wide range of topics including explosions generated by nuclear devices, high explosives and gas and vapour clouds, and partially confined explosions; in addition, damage mechanisms are discussed at some length.

The third survey by Coevert et al. [6] concentrates primarily on work on detonation phenomena as they might be expected to relate to vapour clouds. An interesting example of the uncertainties existing in this area is the conclusion of Munday [7] that detonative combustion is very unlikely in unconfined conditions unless a priming confined or condensed explosive source is ignited.

The present report is directed primarily to work which might help to provide models of the various phenomena which can be grouped under the heading of unconfined explosions. This report also contains some updating of published information previously reviewed in the three surveys mentioned above.

As the expression non-ideal explosion is often used interchangeably with that of deflagration explosion in the literature it may be helpful to note that an ideal explosion is one which can be treated as originating from a point source. Unconfined deflagration explosions are invariably non-ideal, whereas the explosions produced by high explosives are ideal and detonations in gas or vapour clouds may be treated as such.

Unconfined explosions

There are at least four categories under which gas and vapour cloud explosions may be classed. They are respectively BLEVE, deflagration, detonation and physical explosion.

Boiling liquid expanding vapour explosions

This type of explosion is the BLEVE explosion. These are often, though not necessarily always, associated with the transport of flammable cryogenic liquids in tankers either for storage or distribution. A fairly recent example is provided by an explosion in Tewsbury, Massachusetts, U.S.A., involving a semi-trailer tank delivering liquid propane gas to a liquid natural gas (LNG) plant [8]. The truck tank ruptured due to an accidental fire and in the subsequent series of explosions and fires one man was killed and a direct loss of $ 220,000 to plant and fire equipment was sustained.

These explosions occur when a vessel containing liquefied gas suffers mechanical failure. This can occur due to excessive pressure, commonly generated as a result of heating by an external fire. Alternatively, since the mechanical strength of the portion of the vessel exposed to fire will be drastically reduced, the equipment may well rupture below the set operation pressure of any pressure relief devices employed to protect the vessel. Another phenomenon that can occur is that the tank may go 'shell-full' (*i.e.* the liquid can expand to fill the tank). Under such circumstances rupture is probable with any further expansion of the liquid and the absence of adequate pressure relief.

The initial blast occurs immediately on failure and the resultant fire ball and blast debris cause most of the damage. Burning droplets of the liquid involved and debris from the explosion are rained on personnel and equipment and fragments from the vessel may reach distances of up to 600 m [9]. If the explosion occurs at the point of storage or distribution, rather than en route, other vessels containing the material will be present and hence at considerable risk in the ensuing fire.

Deflagrations

The second type of explosion is that of deflagration explosion. Explosive gas or vapour accidentally released mixes with air to form an explosive cloud.

Contact with an ignition source during the period in which its bulk composition lies within the flammability limits can result in a deflagration.

There is some suggestion that Flixborough may well be an example of a deflagration explosion [10]. However, it is worth noting that just as there is vigorous dispute about the causes of this accident [2,11,12], so considerable divergences of opinion still exist as to whether the Flixborough incident involved a detonation or deflagration.

Although the possible causes of this event will not be discussed here, one novel suggestion is that a pressure surge produced by the explosive boiling of a mixture of cyclohexane and water (boiling point 69°C) occurred in reactor 4 disrupting the bridging pipe, when water and cyclohexane (boiling point 80°C) at temperatures greater than 69°C came into contact [12]. This suggestion is mentioned because it indicates one of the unusual types of phenomena that can occur with the highly volatile combustible liquids which are frequently associated with unconfined vapour cloud explosions.

Detonations

The third category of explosion is that of detonation of gas or vapour clouds formed on accidental release of flammable gas or vapour. There are two ways in which a detonation might be initiated. A strong shock may cause thermal initiation or alternatively a detonation might be produced by means of an accelerating flame.

There is at present considerable dispute as to whether or not detonations can occur normally in such clouds, i.e. when high explosives are not the initiating source. There is only one well-documented accident for which a substantial case has been made for explosions involving a detonation [13]. It occurred at Port Hudson, U.S.A. in 1970 on the ignition of a vapour cloud generated by a leak in a liquid propane gas pipe-line. In this particular incident the estimates of near and far field damage indicate that the energy release was equivalent to that of approximately 50 tons of detonating TNT.

Physical explosions

The fourth category of unconfined explosion is provided by the accidental release of either very hot or cryogenic liquids on water. This type of explosion is due to the rate of evaporation of the lower boiling point liquid becoming explosive. Two examples of this phenomenon are provided by the accidental release of liquefied gas or molten metal on water. There are as yet no catastrophic examples of disaster arising from the interaction of liquefied gas and water. However, it may well only be a matter of time until even larger quantities of these materials are being transported (for instance, plans exist to construct and employ 18 million-gallon tankers transport LNG from Alaska to Japan [14]), when the likelihood of a catastrophe will be increased.

Explosions due to the accidental release of molten metal on water or vice versa are not uncommon. A typical example is discussed by Lipsett [15] which was created by the release of molten steel on to water. In this particular incident one man was killed and considerable damage done to the building in which the foundry was housed. Lipsett argues that the damage was caused by a shock wave generated by the explosive heating of the water. Another such accident has occurred recently in Scunthorpe, in a British Steel Corporation foundry, killing 11. Details of this accident can now be obtained in a report [16].

Generally speaking, collated information on particular types of explosion incidents is difficult to obtain. Strehlow's paper on unconfined vapour cloud explosions [4] is the best current source, in which he considers accidents between the period 1930 and January 1972.

Theoretical models and experimental work

Physical explosions

Recently there have been considerable efforts to determine the mechanism of explosions arising from the mixing of liquids with widely different boiling points [17—21]. In this report considerations will be restricted to one of the later and more extensive studies by Anderson and Armstrong [22].

In addition to attempting to analyse a number of accidents, these workers performed various experiments involving molten salts and water in order to elucidate the mechanism of this type of explosion. They showed that the homogeneous nucleation model of Engers and Hartman [19], which involves the super-heating of the cold liquid at the liquid—liquid interface, could not satisfactorily explain their results. Instead they postulated a dynamic impact model for their systems.

This model demands that the liquids are initially mixed in such a way that one liquid becomes entrapped within the other with a gas or vapour phase separating the two. The intervening gas/vapour layer must be thinned or totally collapsed by an external force which propels one fluid into the other, (*e.g.* gravity where one fluid falls some distance into the other) so that the heat transfer rates may become high enough to vaporize a significant fraction of the cold liquid during the short period the two liquids are together. If a large enough fraction is vaporized then an explosion will occur in one liquid/liquid contact. Otherwise smaller vaporizing fractions require multiple liquid/liquid contacts, each contact generating vapour and driving the remaining cold liquid back into the surrounding hot liquid.

This model cannot of course explain the original observations with cryogenic liquids where explosions can occur in stable-layered systems with no external forces. Anderson and Armstrong [22] were unable to determine whether or not there were two basically different types of explosion and mechanisms, or alternatively provide a new mechanistic model to harmonise the different experimental observations. It is interesting to note that dynamic impact models have been invoked in other work [20,21] but the question must be regarded as open at this time.

Anderson and Armstrong [22] have also performed various calculations on the maximum potential work produced by explosions involving hot liquid salts or metal and water. Their results show that up to 40 per cent of the available thermal energy in the hot liquid can be converted into destructive work.

In the case of molten metal/water explosions, this obviously means they are likely to be particularly severe. The position with cryogenic liquids (particularly hydrocarbons such as LNG), however, is less clear although Enger [23] concludes that the total energy released by these explosions is rather small. He also suggests that in a large spill situation there are likely to be many small explosions rather than one large one. If so, this should obviate the danger of dangerous blast waves in air. Further work in this field must be regarded as important, if only because there are many situations in which large quantities of molten metal are used near water. One example is the use of molten metals in liquid cooled nuclear reactors. Such systems are always likely to present the risk of severe physical explosions, the mechanisms for which are still in question.

Boiling liquid expanding vapour explosions

Relatively little work has been carried out on BLEVE. Recently, however, an extensive programme has been completed on the behaviour of rail-road tanks containing liquid propane gas exposed to JP4 fires [24—29]. A number of features of these explosions were examined including the behaviour of the tanks up to the point of rupture, the use of thermal shields to protect the tanks and the fragmentation behaviour of the tanks. Other recent studies include those of Phillips [28] on techniques to protect tank cars from fire by means of an insulating coating, those of Stewart [9], and Baker et al. [29, 30] who have discussed the fragmentation patterns produced in BLEVE explosions. Another study of importance is that of High [31] on the size and duration of the fire ball produced in such explosions.

Deflagration and detonation explosions

For the purposes of this discussion it is simplest to consider these two types of explosion together. The most significant feature of deflagration and detonation is that of blast waves and in the last two decades there has been a vast expansion of work in the field of gas dynamics of explosions. Numerous treatments of the behaviour of blast waves generated under a wide range of conditions now exist [32—34]. Normally, sich solutions are self-similar and require many assumptions about the nature of the system involved. The commonest assumptions are that a perfect gas with constant γ is involved and that any detonation front behaves as a discontinuity surface only, thus allowing the coupling mechanisms between the hydrodynamics and the chemical kinetics to be ignored.

The discussion here will be restricted to work that either adds to the understanding of the physical mechanisms of non-ideal explosions, or alternatively to work aimed at producing simple models.

One of the most recent studies on the measurement of energy release rates from unconfined deflagration explosions is due to Strehlow et al. [35]. These workers have provided a technique whereby data from three pressure gauges placed at the apices of an 'imaginary' equilateral triangle whose centre is the explosion site, may be reduced via the method of characteristics [36] to give the energy release rate $E(t)$. The only major assumption made is that the flow is effectively isentropic so that any shock developed during the deflagration must of necessity be weak. Given this, an 'effective spherical piston' to replace the explosion may be back-calculated allowing the determination of $E(t)$ and also the pressure and flow velocity dependence on line and radial distance, *i.e.* $P(r,t)$ and $V(r,t)$ respectively.

The assumption of isentropic flow will probably be appropriate for most systems. Thus the technique should provide information which characterises explosions and indicates the effects of variation of such parameters as cloud size, nature of combustible material and ignition source etc. However, the suggestion of Strehlow et al. that this be done with a large number of controlled explosions does not appear to have been taken up.

Most of the studies on unconfined explosions to date have involved the use of gas-filled rubber bags and balloons. A typical series of studies of this type was carried out by Woolfolk and Ablow [37,38] who examined the behaviour of stoichiometric mixtures of hydrogen/oxygen with nitrogen as a diluent in spherical balloons of capacity 411 and 2460 l respectively. These were ignited either electrically or by means of a detonator.

Deflagrations were produced with the electrical ignition. These showed a gradual rise of pressure in the near and intermediate field followed by the development of a shock front in the far field. When the 'charges' were ignited by a detonator, ideal explosions (*i.e.* detonations) resulted.

Amongst the most interesting features of their work was the observation that non-ideal blast waves produced when electrical ignition was used, could generate pressures in the surrounding atmosphere that were greater than those produced by an ideal explosion. They were also able to relate the total pressure P for the smaller balloon to a simple form:

$$P = Ar^{-J} \qquad (1)$$

where A and J are constants and r is the distance from the blast wave source at which the pressure is measured. As the results for the larger balloon did not conform with eqn. 1 it is suggested that the scale of experiments is an extremely important factor in determining the decay of pressure waves.

The use of such experiments to determine the behaviour of unconfined deflagrations is open to two major criticisms. Firstly, the bursting of the balloon may well affect the subsequent flame propagation. Secondly, the scale of such explosions tends to be relatively small, the largest capacity balloon

Woolfolk and Ablow [38] used, for instance, was only 1.7 m in diameter. The dangers of applying such results to systems which may be several orders of magnitude larger are obvious, for instance the effect of the interaction of the shock wave with the ground is liable to be quite different.

Unconfined vapour cloud explosions

A most important experimental programme on the behaviour of unconfined vapour cloud explosions was recently initiated by the U.S. Coastguard [39,40]. Its aims are to quantify the explosion hazards associated with spills of large quantities of explosible materials (*e.g.* LNG, liquefied petroleums gases (LPG), and ethylene etc.) and to examine the causes of such explosions in detail.

This programme is still in progress and as yet relatively few of the experimental results are available. Of those that are perhaps the most interesting are observations on the behaviour of spark ignited hydrocarbon/air mixtures contained in 5 m and 10 m radius plastic hemispheres [40]. In no case has transition to detonation been observed, even when ethylene oxide/air mixtures were employed and objects were placed in the hemispheres to generate turbulence. Further tests on the 5 m and 10 m radius hemisphere are contemplated with an analysis of the relationship between flame speed and pressure.

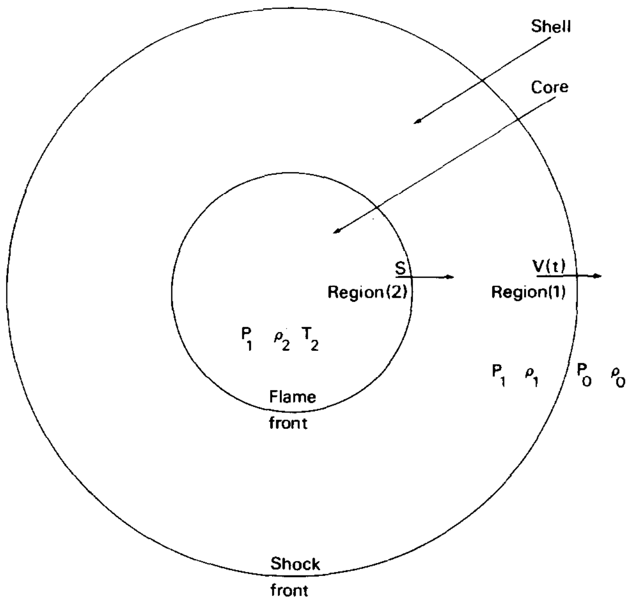
Amongst other work to take place in this programme are studies of:

(a) the behaviour of explosions in a 100 kg container, resulting from the explosive dispersion of liquefied flammable gas
(b) the behaviour of four 15,000 gallon liquefied gas spills on a pond
(c) the adequacy and reliability of various ignition sources
(d) the flammability limits of a variety of materials that might be expected to be involved in such accidents (*i.e.* many liquid hydrocarbons).

One of the most valuable achievements of Phase I of this programme is the production of a qualitative theory of non-ideal explosions by Williams [39,41]

The Williams' model shown in Fig. 1 assumes central ignition due to a point source, and the flame front which develops is considered as travelling at some well defined speed S. An additional assumption is that the pressure waves produced by the flame generate a weak shock travelling ahead of the flame at some velocity $V(t)$ which is a function of time. The final simplifying assumption is that the pressure and the density ρ_1 in the shell between the flame and the shock front (region 1 in Fig. 1) are constant. In Williams' model ρ_1 is set equal to ρ_0/K where ρ_0 is the density of the air at ambient conditions and K is some time-independent constant.

The last assumption has been shown to be reasonable by the work of Kuhl, Kammel and Oppenheim [42]. These workers produced an exact numerical study of the pressure waves generated by a steady flame for self-similar conditions in which the deflagration and shock each travel at constant velocity. The assumption has also been employed by Strehlow in a simplified model for the blast waves generated by constant velocity flames [43]. His results showed



Where P = pressure in regions 1 and 2
ρ = density
S = flame speed
V(t) = shock speed
suffix 0, 1 and 2 = conditions pertaining to ambient regions (1) and (2) respectively

Fig. 1. The Williams model of non-ideal explosions [37,38].

excellent agreement with those of Kuhl et al. [42] for the pressures generated at the flame and shock fronts.

Given this simple model a number of equations for the mass and momentum of the core and shell have been produced (see Fig. 1). Three cases have been considered. The first involves spherical symmetry. The second involves hemispherical symmetry with the assumption that the shock is still spherical with a radius R' but that the other half space is occupied by a non-combustible gas. The third case is for cylindrical symmetry with the assumption that a cloud of height h is bounded below by a rigid base and above by a non-combustible gas.

The equations for the case with spherical symmetry are shown below to give an idea of the simplicity with which this problem can be formulated. The momentum conservation across the shock wave:

$$P = 1 + (1 - K)(\mathrm{d}Y/\mathrm{d}\tau)^2 \quad (2)$$

The overall mass conservation for the sphere of radius R':

$$\theta P X^3 + (Y^3 - X^3)/K = Y^3 \quad (3)$$

The mass conservation for the burned core respectively:

$$X^2 s/K = d/d\tau(\theta P X/3)^3 \quad (4)$$

When θ, K and P are time independent
The similarity solution is:

$$s = \frac{K\theta P\sqrt{P-1}}{(1-K\theta P)^{1/3}(1-K)^{1/6}} \quad (5)$$

where P is the dimensionless pressure P_1/P_0
K is equal to ρ_0/ρ_1 and is a constant less than one
Y is the dimensionless ratio R'/R'_0 of the radius of the shock front R' to its initial value R'_0
X is the dimensionless ratio of the flame radius to its initial value r/r_0
s is the dimensionless flame speed S/a_0
S is the flame speed
a_0 is the Newtonian speed of sound
τ is the dimensionless time
t is the time
θ is the ratio of the ambient temperature to that of the core T_0/T_2

The suffixes 0, 1 and 2 for pressure P, density ρ and temperature T refer to conditions at ambient, in the shell and at the core respectively.

In the case of cylindrical symmetry it is necessary to invoke a nondimensional combustion height α equal to h/R'_0 where h is the height of the planar combustible layer. Also for cases involving cylindrical or hemispherical geometry it is necessary to invoke an efficiency factor η in the conservation equation to account for the effect of the non-combustible gas, *i.e.* the air which acts as one of the boundaries. This factor is defined as the ratio of the actual volume subtended by the shock in the non-combustible gas to the volume of a hemisphere of radius R'. The difficulty in determining η represents the most serious weakness in this approach.

Using this highly simplified model, Williams has obtained a number of interesting results. For example, on the basis of the mass conservation principle, which is expressed in eqn. 3 (for the case of spherical symmetry), the shock strength has a well defined upper limit. Another conclusion is that the flame speed must be an appreciable fraction of the sound speed for a transition to detonation, *i.e.*

$$S > (K/3)\sqrt{(P-1)(1-K)} \quad (6)$$

Williams has also shown that the similarity solution provides useful answers under all conditions except those where substantial acceleration of the flame front occurs over acoustic time scale. The acoustic time scale is that for propagation of a sound wave over a distance equal to the shock radius.

A problem which has been examined recently by Sivashinsky [44] could almost be regarded as the inverse of one examined by Williams. It concerns the behaviour of a converging spherical flame front. The equations are set up and solved for the frontal propagation velocity of a spherically symmetric flame propagating to a focusing centre. This work shows that there are three solutions corresponding to Lewis number less, equal to and greater than one respec tively. The Lewis (or Lewis—Semenov number) is the ratio of the energy transported by conduction to that transported by diffusion.

For Lewis numbers less than one, the flame tends to extinction, while for a Lewis number equal to one the flame propagates at a constant speed to the centre. Only in the case of Lewis numbers greater than one will the flame accelerate. For the latter case it has been shown that when the dimensionless activation energy E/RT (where E is the activation energy, R the gas constant and T the burnt gas temperature) is much greater than unity, the flame propagation will become unstable. In that event the flame will enter a self-oscillation regime about some constant value as a function of time.

The last possibility that the Lewis number is greater than one is fairly unlikely. In most systems the Lewis number will be slightly less or equal to unity and only in systems containing significant amounts of hydrogen or helium is it likely that the Lewis number will be greater than unity [45]. Also, in most systems involving hydrocarbons the dimensionless activation energy E/RT will be large, normally greater or equal to ten [46]. This means that an accelerating flame would rarely be expected to arise and even if it did, the flame would probably enter the oscillatory regime.

A situation equivalent to the case of a focusing spherical flame might be expected to occur in accidents where flammable clouds suffer ignition at the edge. The rationale for this lies in the fact that such clouds may be expected to become increasingly fuel-rich towards the centre and although burning velocities usually reach their maximum values slightly on the rich side of stoichiometry [47], there may come a point where propagation 'round' the cloud could become greater than towards the centre. In that event the flame front would develop into a spherical flame propagating inwards.

Since Williams [39,41] has shown that detonations due to a thermal mechanism are fairly unlikely and Sivashinsky's work [44] indicates that detonations due to an accelerating flame mechanism are also likely to be uncommon, it would seem detonations might be expected to be rare. The only situations not investigated are those where obstacles are present. In that case, detonation might arise either due to focusing of any shock waves generated or turbulence generated by the obstacles leading to flame acceleration. In those situations where the ignition source is a high explosive, detonation may well arise but such ignition sources are likely to be rigorously excluded from situations where accidental release of flammables are likely.

Conclusions

This survey indicates that there is a major need for more experimental and theoretical work on non-ideal explosions. The incidents at Flixborough and Beek have further shown that the economic significance of these events is very great. The frequency of these events may well increase since the economic pressure to store, handle and transport even larger quantites of such materials is extremely powerful [48].

At the present, Williams' approach for modelling these situations appears to be most simply applicable of those available. However, there is considerable need for better models, especially ones which can take into account the effect of obstacles. In particular, it is important that experiments that are carried out are performed with the wider view of giving information which can be generalised rather than mainly providing information for specific problems as has perhaps been the tendency in the past.

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