THE EFFECT OF CONDITIONS PRIOR TO LOSS OF CONTAINMENT ON FIREBALL BEHAVIOUR

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The failure of a vessel containing a flammable liquid with a vapour pressure greater than atmospheric will lead to flash evaporation of some of the liquid and the formation of a rapidly expanding cloud of flammable vapour, liquid droplets and air. The ignition of such a cloud is likely to lead to a fireball. The mechanisms of cloud formation are discussed with reference to the initial momentum created by flash evaporation and the effect of the initial state of the liquid. Correlations for fireball size, duration and radiation output are given and the effects of initial conditions on these are considered.

INTRODUCTION

The total failure of the containment system for a flammable liquid, although an unlikely event, may arise from a variety of causes - corrosion, weld failure, mechanical impact, the effects of heat from an external fire. If a massive release of flammable liquid is ignited the consequences may range from a prolonged but localised fire to a major fireball or vapour cloud explosion depending on the various factors involved, particularly the vapour pressure of the released liquid.

The chemical and petroleum industries have long experience of the fire problems resulting from the accidental release of large quantities of hydrocarbons with boiling points above atmospheric temperature, but the introduction of the large scale transport and storage of LNG and LPG under refrigerated or pressurised conditions led to new kinds of fire and explosion problems through a combination of high liquid volatility and large scale of use.

Consider the spillage of a volatile liquid such as petrol in the open air: the liquid will flow under gravitational forces and form a plume of vapour by evaporation from the pool surface; the plume size (to the lower flammability limit concentration contour) prior to ignition will depend on the pool surface area, heat transfer rate to the pool from the environment, ignition delay, and meteorological and topographical conditions. Once ignited at a point, flame spread through the plume and across the liquid surface is likely, via the regions where the concentration of fuel vapour lies within the flammability limits, at flame speeds of the order of 5 m/s.

The large scale spillage of a refrigerated liquid, stored at a

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temperature giving a vapour pressure close to atmospheric pressure, is conceptually similar to the above description. Major differences of detail are the greater boil off rates caused by the greater pool/environment temperature differences and the possible effects of scale. It needs to be established whether these factors, by creating more turbulence or larger plumes, will lead to more rapid flame spread or other hazards: large-scale field trials on this problem conducted by Shell at Maplin (1) should yield valuable data.

The release of liquids from pressurised storage, however, introduces a new set of problems because the mechanisms of dispersion of the released liquid are more violent and the ensuing combustion may be orders of magnitude more rapid. Consider the failure of a pressurised vessel under the influence of an external fire: the vessel starts off with a certain strength but, under the heating effects of the fire, the shell weakens and the pressure (P_S) required to produce failure decreases; the heating effects are not necessarily uniform and failure will occur at the weakest part of the shell. The initial vapour pressure $(P_V)_o$ of the liquid is substantially less than $(P_S)_o$ but, under the heating effects of the fire, the vapour pressure rises and failure occurs when $P_V > P_S$. If a relief valve is fitted to the system, set to operate at P_r but with an inadequate capacity to cope with the boil off rate, then P_V can rise above P_r; a correctly sized relief valve would cause P_V to stabilise at $P_V \simeq P_r$. Thus, the characteristics of any relief valve fitted to the system also affect the failure pressure.

It is clear from this description that the pressure at which the system fails is a complex function of its initial conditions, the heating effects of the fire and the reaction of the system to these effects. The vapour pressure of the liquid at the time of failure must therefore be regarded as a variable when considering the subsequent behaviour (dispersion and combustion) of the released substance.

In addition, the mode of vessel failure may also vary with these factors. A container failing at a high pressure, relatively unweakened by heat, may burst violently producing a virtually instantaneous release of its entire contents; a container failing at a lower pressure due to local weakening may split in a localised area only, producing a sustained discharge of liquid or vapour or a two phase flow. In the latter case, the considerations discussed by Fletcher (8) would apply.

The remainder of the paper will be concerned with the situation following the bursting of a pressurised container and the instantaneous release of a large mass of flammable liquid to atmosphere.

MECHANISM OF FLAMMABLE CLOUD FORMATION

The bursting of a vessel containing a liquid with a vapour pressure greater than atmospheric leads to rapid flash evaporation of some of the liquid and the fragmentation of the remaining liquid; the higher the proportion of liquid converted to vapour by flash evaporation, the greater will be the fragmentation of the remaining liquid, so that a higher proportion of the liquid phase is dispersed as an aerosol rather than as large droplets that settle rapidly to the ground.

The rapid formation of vapour by flash evaporation creates an expanding cloud of vapour with a pressure above atmospheric; if the rate of formation

of vapour is sufficiently high, blast waves will be produced. The acronym BLEVE (boiling liquid expanding vapour explosion) refers specifically to this phenomenon, which can occur with any liquid (eg water, chlorine) under appropriate circumstances; however, it is sometimes loosely used to refer to the bursting of a vessel as a result of an external fire and the combustion of a released flammable liquid in a fireball (see below).

As the cloud expands it entrains air and its radial velocity decreases, through momentum conservation principles. At later stages, other dispersion forces begin to predominate; gravitational slumping of the cloud occurs, followed by dispersion by wind effects. In these later stages the dispersing cloud of vapour behaves in a similar way to the plume of vapour from an evaporating pool (see above). Thus, ignition delay critically affects the behaviour of a burning cloud since zero ignition delay (as would occur with failure induced by an external fire) would lead to the rapid burning of a highly turbulent cloud whereas a significant ignition delay would lead to combustion behaviour more akin to that of a refrigerated liquid.

Two models of cloud formation following the release of a pressurised liquid have recently been compared by Roberts (2). One model, derived by a method suggested by Hardee and Lee (3), is based on a conservation of momentum approach with the momentum created by the release of the liquid appearing explicitly; the other model, derived by Maurer et al (4), is based on a turbulent diffusion model and the initial conditions of the stored liquid do not appear explicitly. The two models give somewhat similar predictions of rate of cloud growth for releases of about 100 kg and both models have received experimental verification in this region. However, they predict different scaling effects as release size is increased.

The former approach will be considered in more detail here. For a hemispherical cloud, formed by a release at ground level, it predicts

$$r = \left(\frac{4\alpha M_R t}{\pi \rho_A}\right)^{1/4} \qquad - (1)$$

where r = cloud radius at time t after release, M_R = mass of release, ρ_A = density of air and α = momentum of release per unit mass. Manipulation of (1) gives expressions for rate of expansion of the cloud, cloud volume and mean concentration as required.

According to reference (3), values of α for propane are 120 m/s for a vapour pressure of 0.5 MPa and 220 m/s for a vapour pressure of 1 MPa.

The time required for the mean concentration to drop to the lower flammability limit (t^1) for propane is given by

$$t^1 = \frac{35}{\alpha} M_R^{1/3} \qquad - (2)$$

If α = 220 m/s, t^1 = 1.6 s for M_R = 1000 kg and t^1 = 7.4 s for M_R = 100,000 kg. Relatively short ignition delays may therefore allow sizeable portions of the cloud to be diluted below the lower flammability limit.

Jagger and Kaiser (5) have obtained a relationship for the time (t_g) at the transition between domination of dispersion by the original momentum of the system and domination by gravitation effects, using the model described in reference (4):

$$t_g = 10\ M_R^{-1/3} \qquad - (3)$$

However, using the model based on Hardee and Lee's method (3) gives a relationship

$$t_g = 0.05\,\alpha \qquad - (4)$$

This illustrates one of the important differences in scaling predictions between the two models since eq (3) predicts a rapid decrease in duration of the first stage of the dispersion process as release size increases whereas eq (4) predicts no such effect.

Intuitively the Hardee and Lee approach seems more relevant since it incorporates more of the known factors that influence the system in the term α; also, eq (3) predicts very small values of t_g for large values of M_R.

For α = 220 m/s, eq (4) predicts t_g = 11 s while from eq (2) t^1 = 11 s is given by a release size of M_R = 324,000 kg for this value of α. Thus, for these conditions the equations predict that for releases up to about 300 tonnes the momentum driven phase of the dispersion process is the dominant one throughout the period in which ignition is possible.

For α = 120 m/s, this conclusion would apply for releases up to about 9 tonnes illustrating the effect of initial conditions on the whole process of dispersion and ignition.

As stated above, the expansion of the cloud itself, in the absence of ignition, can lead to blast effects and radial velocities initially as high as 200-300 m/s. The ignition of a rapidly expanding cloud of flammable vapour/air mixture will lead to very rapid combustion rates. Maurer et al (4) have measured blast effects and flame speeds following the ignition of such an expanding cloud following releases of 450 kg of propylene; the measured blast effects were all attributable to the cloud expansion process and flame speeds up to about 50 m/s, as measured.

The blast effects of spreading flames begin to be noticeable at flame speeds of about 50 m/s and serious at flame speeds of 200 m/s. The above experiments were therefore approaching the region in which vapour cloud explosions become a possibility through the linking of a combustion wave to the rapidly expanding cloud surface. The factors that cause vapour cloud explosions, through the acceleration of flame speeds of 5 m/s or so to 200 m/s, are not well understood but several of the candidate explanations (intense turbulence in cloud, high velocity gas flows, dispersed fuel particles able to absorb thermal radiation) are present in this situation.

What is reasonably certain is that the ignition of an expanding cloud of fuel/air mixture will lead to a fireball, that is to say, the combustion of the cloud in a single rapid event which gives the appearance of an expanding ball of flame which lifts off from the ground under the effects of buoyancy forces and travels upwards as a rapidly cooling ball of products. The hazards

from a fireball derive from flame spread and the pulse of thermal radiation that results.

FIREBALL CHARACTERISTICS

Available data for fireball behaviour have been reviewed in (2) and the following conclusions were drawn:

Mass of fuel in fireball

In (6) it is stated that where the theoretical flash evaporation from a liquid (f) exceeds 35%, all the released fuel burns in the fireball but at lower percentages some burns in a pool fire rather than in the fireball. If M_R is the mass of liquid released and M is the mass that burns in the fireball then, as an approximate guide:

$$f = 0 \quad M/M_R = 0$$

$$f \geqslant 35 \quad M/M_R = 1$$

$0 < f < 35$ Estimate M/M_R by linear interpolation between above limits. This transition is of considerable interest in predicting fireball behaviour and more information on it would be valuable.

Maximum fireball size

The maximum diameter of the equivalent sphere (D_{max}), based on the projected area of a fireball is relatively insensitive to fuel type and to the mechanism of cloud formation. Fireballs of the type considered above and fireballs formed from quiescent clouds of vapour have similar relationships for D_{max} (even though other characteristics may differ considerably) as follows:

$$D_{max} = 5.8\ M^{1/3} \qquad - (5)$$

D_{max} is in metres, M = mass of fuel in fireball, kg.

This equation provides a reasonable estimate of the available data, including values of M up to 5000 kg and of a theoretical relationship derived from thermodynamic considerations. The theoretical approach shows that the coefficient in equation (5) is insensitive to final fuel/air ratios etc and it is thought that equation (5) can be extrapolated with some confidence to large values of M.

If a fireball forms at ground level, its form prior to lift off will be hemispherical in which case the following relationship will apply:

$$(D_{max})_H = 7.3\ M^{1/3} \qquad - (6)$$

In terms of determining the area covered by flame at ground level, eq (6) gives the worst case and also it represents a probable situation for storage at ground level. Typical values of $(D_{max})_H$ from (6) are

M (kg)	$(D_{max})_H$ (m)
1,000	74
10,000	159
100,000	343

These values therefore represent the diameter of a circular area affected by flame spread, with its centre at the point of release; any ignition delay and cloud drift downwind would affect this estimate as described above.

Fireball duration

This is a complex topic because it involves the time of rapid initial combustion, the time to completion of combustion as final mixing of fuel and air takes place, the cooling of the fireball by radiation and the buoyancy effects on the fireball causing lift off.

For the type of situation considered in this paper the time of the initial combustion is given approximately by eq (2) and is therefore dependent on α ; at this time the fireball has grown to more or less full size and is at peak radiation intensity. Thereafter its size stays roughly the same as its mean temperature decreases both by entrainment of cool air and heat loss by radiation. Its duration, as an effective source of thermal radiation, is given approximately by

$$t_d = 0.45\ M^{1/3} \qquad - (7)$$

where t_d is in seconds. This relationship is derived from data from experiments with values of M up to 30 kg and from a simple theoretical model and appears to be relatively independent of α .

Fireball lift off times (t_L) are correlated by the expression

$$t_L = M^{1/6} \qquad - (8)$$

so that for $M < 120$ kg $t_d < t_L$ and for $M > 120$ kg $t_d > t_L$. The different indices for M in eq (7) and (8) result from the different controlling mechanisms. In terms of predicting the thermal radiation hazard, eq (7) seems the more appropriate means of fixing the time scale of the event.

Radiation output

The total energy release in the fireball is MH where H is the heat of combustion of the fuel. Some of this energy remains in the combustion products as the fireball lifts off and some is radiated from the fireball.

The available data (2) suggest that the fraction (F) radiated from the fireball over the timescale defined by eq (7) is in the range 0.2 - 0.4 with a systematic increase in F as the initial vapour pressure of the system increases. This is consistent with the present analysis, since an increase in vapour pressure increases α and hence increases the rapidity of mixing of fuel and air. This is turn results in a higher combustion rate and a hotter flame. At the lower end of the vapour pressure range the fireball is more akin to a pool fire flame with flame colours of red/orange/yellow, whereas at the higher end of the range flame colours are bright yellow/white.

Values of F have been correlated in terms of P_v (vapour pressure, MPa) in (2) and this correlation gives a value of F = 0.3 for a system failing at about 1.5 MPa, a typical relief valve setting, and a value of F = 0.4 for a system failing at about 5 MPa. However the available data are rather scanty and more estimates of F would be valuable.

It is therefore possible to characterise the thermal radiation output

from the fireball in terms of a square wave pulse of amplitude FMH/t_d and duration t_d and to apply the inverse square law to determine the radiation intensity at points outside the fireball. This approach is analogous to the one recommended for flarestack calculations (7).

It is also possible to construct a dynamic model for fireball behaviour, taking account of variations with time of size, surface heat flux etc; although such a model is of undoubted scientific interest and vital to a proper understanding of fireball behaviour and scaling laws, as far as applications are concerned the response of exposed objects to thermal radiation is not particularly well documented and the assumption of a square wave pulse is usually necessary to predict target response.

Since surface heat flux values are often quoted it is of interest to record what the above range of values of F corresponds to in these terms. Assuming a fireball that grows instantaneously to a diameter D_{max} and remains at that size for a period t_d with a surface heat flux Q_o and an equivalent flame temperature T gives the following comparison:

F	Q_o (kW/m^2)	T (^{o}C)
0.3	277	1200
0.4	370	1320

For pool fire studies, values of Q_o up to about 250 kW/m^2 and values of F up to 0.4 have been estimated. Thus fireballs and pool fires have certain similarities although the former have much greater combustion rates than the latter and are probably higher temperature sources.

There are instances in the literature where values of Q_o of 1200 kW/m^2, corresponding to the adiabatic flame temperature of around 2100^{o}C, are quoted for fireballs; such values are regarded as unrealistically high.

PREDICTION OF RANGES TO VARIOUS THERMAL RADIATION EFFECTS

The above analysis predicts that a fireball will give rise to a thermal radiation flux Q, at a distance L from the fireball centre, given by

$$Q = \frac{FHM}{4\pi L^2 t_d}\ a$$

where a is an atmospheric transmission coefficient which allows for the effects of attenuation of the radiation by the earth's atmosphere. The value of a depends on atmospheric conditions (humidity etc), source characteristics (spectral distribution of radiation energy, hence source temperature) and distance from the source.

Typical values of a for the conditions of interest are a = 0.75 at 50 m, a = 0.61 at 500 m (12). The attenuation effect is therefore significant.
Some examples of response to thermal radiation are given in Table 1 in terms of the relationship between flux needed to achieve a certain effect and the duration of exposure. Considering a release of 100 tonnes of a fuel with H = 45 MJ/kg and f $>$ 35% gives the following estimates (taking a = 1).

Fireball radius (hemisphere)	171 m
Fireball duration	21 s
Flux at blister threshold	6 kW/m^2

Flux at cellulose ignition threshold 33 kW/m^2
Flux at 1% lethality threshold 19 kW/m^2
Flux at 50% lethality threshold 34 kW/m^2

The values of L at which these flux levels would be achieved are as follows:

Values of L(m) for various values of F and Q

F \ Q	33	19	6
0.3	395	520	925
0.4	455	600	1070

It can be seen that predicted distances to the various effects are quite sensitive to the assumed initial conditions of storage (affecting F, via $\propto$) and the type of effect considered. These distances would be reduced by allowing for atmospheric attenuation of the radiation.

The 1% and 50% lethality figures are derived from studies of the effects of nuclear blasts and therefore relate to a large exposed population occupied on random tasks. The other data are derived from laboratory studies. The blister threshold values relate to bare skin exposed to a steady radiation pulse for the specified time.

A number of measures can reduce the severity of thermal radiation effects, eg running away, seeking concealment, so that the effects of a pulse of thermal radiation on an exposed population can vary widely from one situation to another; for example, holidaymakers sunbathing on a beach are more at risk than normally clad people on a chemical plant with ample cover to shield themselves from radiation effects.

CONCLUSIONS

The failure of a container pressurised by the vapour pressure of its liquid contents may occur over a wide range of vapour pressures, at a value depending on details of the system such as cause of failure, relief valve provision etc.

The ignition of flammable liquid from such a failure is likely to lead to a fireball. The vapour pressure of the liquid at the time of failure will affect the proportion of the release entering into the fireball, the combustion rate, the probability of a vapour cloud explosion occurring and the thermal radiation output of the fireball. Some of these effects can be estimated quantitatively but not all of them.

The conditions of a system prior to failure therefore have important effects on the range of effects of the resultant fireball.

TABLE 1 - Effects of thermal radiation at two different exposure times (linear interpolation on a log/log plot is permissible)

Effect	Heat flux required to produce effect (kW/m^2) 4 s exposure	20 s exposure
Blistering of bare skin (9)	20	6
Pilot flame ignition of cellulosic material (10)	66	34
1% lethality (11)	66	20
50% lethality (11)	117	35

SYMBOLS USED

a = fraction of radiation transmitted by the atmosphere

D_{max} = diameter of a sphere of equal projected area to fireball at maximum size

$(D_{max})_H$ = equivalent diameter for a hemisphere

f = percentage theoretical flash evaporation from liquid

F = fraction of heat release due to combustion that is radiated from the fireball

H = heat of combustion of fuel in fireball

L = distance from fireball centre

M = mass of fuel in fireball

MR = mass of liquid released from containment

P_r = operating pressure of relief valve

P_s = internal pressure required to produce failure of a container

P_v = vapour pressure, subscript o indicates initial value

Q = heat flux at a distance L from fireball centre

Q_o = heat flux at fireball surface

r = cloud radius

T = flame temperature

t = time from release

t_d = duration of a fireball as an effective source of thermal radiation

t_g = time at transition between control of dispersion by momentum effects to control by gravitational effects

t_L = fireball lift off time

t^1 = time required for mean concentration in cloud to drop to lower flammability limit

α = momentum of release due to flash evaporation, per unit mass

ρ_A = density of air

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THERMAL RADIATION HAZARD FROM FIREBALLS

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Small scale fireballs were made by igniting elevated hemispherical detergent bubbles filled with butane and with natural gas, in the range 100 to 800 ml. Surface temperatures were measured by two-colour pyrometry from colour cine films of the fireballs. Fireball diameter increases at a constant rate during combustion; both diameter and elevation are dependent on the cube root of the mass of flammable gas. The ranges at which people will be severely burnt from unconfined vapour cloud fireballs and BLEVEs are correlated with mass of flammable to the 0.4 power.

INTRODUCTION

Fireballs are clouds of burning gas or vapour, frequently elevated, which emit intense thermal radiation over considerable ranges. A vapour cloud which is enriched above the upper flammable limit will not explode; upon reaching a source of ignition, flame will spread around the periphery where there is enough air to dilute the vapour and bring it within the flammable range.

Shortly after ignition, the hot combustion shell will be sufficiently buoyant to cause the fireball to rise; thereby increasing the range of hazardous radiation. Air enters the fireball due to its thermally expanding shell and its rise. Thus the size and elevation of fireballs will increase during combustion and the fireball becomes extinct by breaking up into smaller pockets of gas, some of which may still be burning. Soot is produced during combustion of hydrocarbon fireballs, causing luminous flames with an emissivity of unity. Soot is produced also when natural gas clouds ignite to form fireballs; but the flames are not totally luminous and the average emissivity of the fireball surface will be less than unity.

Boiling Liquid Expanding Vapour Explosions (BLEVEs) which occur when a liquefied flammable gas container bursts as a result of being engulfed in fire, produce aerial fireballs; but the initial cloud contains a significant burden of aerosol droplets so that the tendency to produce soot is increased.

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