DANGEROUS CLOUDS, THEIR GROWTH AND PROPERTIES

V. J. Clancey
Dr. J. H. Burgoyne & Partners, London

A vapour cloud grows by diffusion acquiring a Gaussian concentration distribution. Its maximum explosive potential occurs when the concentration at the centre equals the upper flammable limit. Its damage potential is usually calculated from a TNT equivalent; a possibly preferable method is based upon the production of a maximum pressure of 69 kN/m^2 (10 psi) at the periphery. Propagation laws for shock waves in air enable damage at a distance to be estimated.

INTRODUCTION

The disaster at Flixborough was due to the explosion of a massive cloud of inflammable vapour following an accidental release. The explosive potential of such a cloud depends upon the quantity of vapour in the cloud which is available for rapid combustion. This changes as the cloud moves downwind.

Gaussian distribution of concentration

When a large quantity of vapour is released instantaneously it forms a cloud which develops ultimately into a hemisphere in which the vapour concentration assumes a Gaussian distribution of the form

$$\chi_{(r)} = \frac{2Q}{(2\pi)^{3/2}\,.\,\sigma^3} \exp\left[-\frac{r^2}{2\sigma^2}\right] \quad \ldots \quad (1)$$

assuming isotropic conditions and that the release was near ground level over a flat terrain.

The first term is the concentration at the centre, χ_o, so that

$$\chi_{(r)} = \chi_o \exp\left[-r^2/2\sigma^2\right]$$

and

$$\chi_o = \frac{2Q}{(2\pi)^{3/2}\,.\,\sigma^3}$$

Quantity of vapour in an annulus

The quantity of vapour in the annulus between r and $(r+dr)$ is

$$Q' = 2\pi r^2 \chi_o \exp\left[-r^2/2\sigma^2\right] dr \quad \ldots \quad (4)$$

Integrating (4) between $r = 0$ and $r = \infty$ gives

$$\int_0^\infty 2\pi r^2 x_0 \exp[-r^2/2\sigma^2]\, dr$$

$$= (2\pi)^{3/2} \sigma^3 x_0 / 2$$

$$= Q$$

Hence the expression in (4) may be integrated between any chosen limits to obtain the absolute quantity of vapour in the region between radii r_1 and r_2

The cloud can be uniquely specified by the total amount of vapour, Q and the standard deviation, σ

The definite integral of (4) cannot be obtained analytically but may be obtained by the use of published tables for the normal distribution.

It may be noted that the distribution of vapour in the cloud (as distinct from its concentration along a radius) is not Gaussian as can be seen by calculating the second and fourth moments about the mean of a spherical cloud and deriving the kurtosis coefficient

$$\mu_2 = \int_0^\infty r^4 \exp[-r^2/2\sigma^2]\, dr \Big/ \int_0^\infty r^2 \exp[-r^2/2\sigma^2]\, dr$$

$$= 3\sigma^2$$

$$\mu_4 = \int_0^\infty r^6 \exp[-r^2/2\sigma^2]\, dr \Big/ \int_0^\infty r^2 \exp[-r^2/2\sigma^2]\, dr$$

$$= 15\sigma^4$$

$$\beta_2 = \mu_4/\mu_2^2 = 15\sigma^4/9\sigma^4 = 1.6$$

Since β_2 is much less than 3 the curve is markedly platykurtic, or flattened and spread-out. This follows, of course, from the fact that the volume of an annulus increases as the square of the radius.

Maximum available for combustion

If x_u and x_l are the concentrations at the upper and lower flammable limits it can be shown that the maximum quantity of flammable mixture occurs when the concentration at the centre is x_u or when

$$x_0 = x_u$$

Substituting from equation (3)

$$x_u = 2Q/(2\pi)^{3/2} \sigma_m^3$$

$$\sigma_m = \{2Q/(2\pi)^{3/2} x_u\}^{1/3} \quad \ldots \ldots \ldots \quad (5)$$

Radius of combustible zone

Having obtained σ_m the standard deviation, when the cloud presents the maximum hazard, it is possible to find the radius r_l at which the concentration is at the lower flammable limit,

$$\chi_l = \chi_o \exp\left[-r_l^2/2\sigma_m^2\right]$$

$$r_l = \left[2\sigma_m^2 \log_e(\chi_u/\chi_l)\right]^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Integral at maximum hazard

Substituting $\chi_o = \chi_l$ and $\sigma = \sigma_m$ in expression (4) and integrating between the limits $r = 0$ and $r = r_l$ will give the quantity of vapour available for combustion when the cloud presents its greatest hazard.

$$F = \int_0^{r_l} 2\pi r^2 \chi_u \exp\left[-r^2/2\sigma_m^2\right] dr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

In order to compute this, e.g. by Simpson's rule, it may be noted that it may be rewritten in the form

$$F = \int_0^{r_l} \left(2Qr^2/\sigma_m^2\right) \left\{\frac{1}{\sigma_m\sqrt{2\pi}} \exp\left[-r^2/2\sigma_m^2\right]\right\} dr \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

where the expression in curly brackets is the normal distribution of which the ordinates are tabulated in the statistical literature.

Thus the maximum potential of the cloud may be determined in terms of the quantity of vapour released and the upper and lower flammability limits.

Position of cloud

The position of the centre of the cloud at this time may be estimated by assuming that it originates as a point source and adopting Sutton's equation (1) for diffusion of an instantaneous cloud originating at a point.

The familiar Sutton equation is

$$\chi = \frac{2Q}{\pi^{3/2} C^3 (ut)^{3(2-n)/2}} \exp\left[-(ut)^{(n-2)} \cdot r/C^2\right] \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

Values of standard deviation and distance from origin

Comparison of equations (1) and (9) gives

$$\sigma = C(ut)^{(2-n)/2}/\sqrt{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

If linear dimensions are in metres the values for the constants for neutral atmospheric conditions are C = 0.14 and n = 0.25. Inserting these values in (10) gives

$$\sigma = 0.1\,(ut)^{0.875}$$

Since u is the mean wind velocity and t the time from release, (ut) is the distance of the centre of the cloud from origin $= x$

$$\sigma = 0.1\,x^{0.875}$$

$$x = (10\sigma)^{1.14} \quad \ldots \ldots \quad (11)$$

At maximum potential $\sigma = \sigma_m$ given by equation (5) so the position of the cloud and the ground region lying under the flammable zone are defined by x measured downwind from the source and a radius given by h_l in equation (6).

It is of interest to note that x is independent of the wind velocity. It depends only on Q and the upper flammable limit.

Typical value of F/Q

Evaluation of the equations for a typical vapour, such as a hydrocarbon, for which the ratio of upper to lower flammable limits is in the range 4-6, shows that $F/Q = \frac{2}{3}$ approx., that is a maximum of about two thirds of the total release is available for combustion.

Growth of cloud prior to maximum hazard stage

Before the maximum state is reached the quantity in the flammable range increases. Initially it may be taken to be zero. If ignition occurred immediately on release (provided there was no turbulent mixing by jet effects) the cloud would burn as a diffusion flame around its periphery.

The growth of the cloud may be followed by integration from the Sutton equation. However for most practical purposes an approximation for the quantity of vapour within the flammable limits may be obtained by assuming that it follows a straight line path from zero at origin to the value given above at the maximum point. Thereafter the quantity falls off fairly rapidly.

EXPLOSIVE POTENTIAL

Flixborough and similar accidents have shown that when a large cloud of inflammable vapour is ignited it can produce an explosion with damaging pressure effects. It seems certain that for this to occur the cloud must be large - tonnage quantities. Smaller clouds produce a fire-ball with little or no pressure effects. There is no clear indication of the dividing line between the two sizes. It is probably several tons.

No satisfactory explanation has been put forward for the mechanism whereby pressures are produced in a burning unconfined cloud. It can be shown that a fast moving flame front produces a pressure but there is no theoretical or practical study to explain how a flame front may accelerate to a velocity sufficient to yield pressures of the order experienced in the accidents.

The TNT equivalent

To overcome this deficiency the damage potential of a cloud is generally assessed by the so-called TNT equivalent. A weight of TNT, which generates 1.1 kcal/gram on explosion, is calculated such that its energy is equal to the available combustion energy of the cloud.

Since most hydrocarbons produce on combustion about 10 kcal/gram the TNT equivalent would be about 10 times the weight of vapour in the cloud. Experience has shown that this is a gross overestimate by a factor of perhaps 20 x or more. An efficiency factor of 0.04 has been suggested by Brasie and Simpson (2) on the basis of the damage caused in several accidental explosions.

Over-estimation of damage under cloud

The most serious defect of the TNT equivalent method is that it gives a completely misleading estimate of the damage to be expected in the area enveloped by the cloud. TNT detonates. This implies extremely high pressure shock waves at short distances with complete destruction of practically everything within the area covered by the cloud. This does not occur with a vapour explosion. Many relatively weak structures are found standing after the explosion. In fact there is very strong evidence that a vapour cloud does not detonate.

Separate damage regions within cloud and external

Examination of the damage at Flixborough and elsewhere shows that there are two regions to be distinguished : the region enveloped by the cloud and the region beyond the periphery of the cloud.

In the region enveloped by the cloud the general degree of damage suggested overpressures of a few tens of pounds per square inch where the TNT equivalent would have indicated pressures of hundreds of pounds per square inch. There were a few "pockets" of higher pressures - up to perhaps 500-700 kN/m^2 (70-100 psi) - due presumably to local effects asa result of confinement or implosion - but these were still well below detonation pressures.

At the periphery of the cloud the damage was consistent with a pressure of about 69 kN/m^2 (10 psi) which then propagated outwards in accordance with the well-established laws for the propagation of a shock wave in air.

Explosion of 10 kg. of propane

As an example we will consider the effects of an accidental release of 10^4 kg. (10 tons) of propane.

If this were mixed with air uniformly to form a hemispherical cloud in stoichiometric proportions it would form a cloud of radius 41.5m and have a TNT equivalent of 10^5 x E kg. where E is the efficiency factor.

Taking E = 0.04, the suggested value, this would imply pressures in excess of 140 kN/m^2 (20 psi) in a region 60m across with complete devastation and a crater 25m across - effects which are certainly not produced by the explosion of a cloud of this size.

Over-pressures at a distance

The pressures to be expected at greater distances on the basis of the TNT equivalent are plotted in Fig. 1.

Using equations (5) and (6) we obtain σ_m = 18.8m and r_0 = 31.3m. This means that initially the periphery of the combustible portion of the cloud would be at a radius 31.3m from its centre. From equation (11) the centre would be 390m from origin.

During combustion the cloud expands by a linear factor of about 2 so that when the flame front reaches the periphery the radius is now about 60m.

We now postulate that it produces an overpressure of 69 kN/m^2 (10 psi) at this expanded radius and on this basis calculate the outward propagation. The result is also plotted in Fig. 1.

The mechanism whereby the pressure is produced at the periphery is indicated by Kuhl, Kamel & Oppenheim. Their relationships suggest that the flame speed must be about 40m/sec, to give 10 psi. Presumably this is effected partially by the expansion of the combustion products and partially by a self-accelerating process. Possible mechanisms will be discussed elsewhere.

Pressures at shorter distances

It is to be expected that acceleration of the flame speed will be exponential. In that case the pressure at distances less than the expanded radius of the cloud would be represented approximately by the broken line in the figure. The peripheral pressure from smaller or larger clouds would lie along this line or its extension.

Since the diameter of the cloud and its explosive potential is proportional to the cube root of the weight of vapour the peripheral pressure is relatively insensitive to changes in weight. As an example the curves for 5 x 10° gram (5 tons) and 2×10^7 gram (20 tons) of propane have also been plotted.

For these reasons it seems reasonable to take 69 kN/m^2 (10 psi) as the peripheral pressure in assessing the maximum potential of a cloud unless there are reasons to believe that the quantity released and capable of forming a continuous cloud is an order of magnitude larger than this example.

Pressures within the cloud

The broken line, between zero and 10 psi in the figure may be taken as an indication of the build-up of pressure as the flame front advances. It probably overestimates pressures, particularly at the lower end, since it has been established that small clouds produce little or no pressures.

On the other hand locally pressures may be greatly in excess. In a built-up area, and particularly in a chemical production complex, there are generally ample opportunities for higher pressures to be developed as a result of confinement, reflection of shock waves, and implosions. Experience suggests that these local pressures may be as much as 700 kN/m^2 (100 psi).

Extreme range of combustible cloud

The cloud ceases to contain any combustible mixture when the concentration at the centre $x_o = x_\ell$, the lower flammable limit.

If σ_i is the standard deviation when the cloud becomes inert, from equation (5)

$$\sigma_i = 30m.$$

and the position of the centre x_i measured from origin is from equation (11)

$$x_i = 667m.$$

It can be shown that during the travel of the cloud to this position the periphery of the flammable zone does not pass the point $x_i = 667m.$ Thus the cloud cannot be ignited by a source of ignition lying at a greater distance than this.

The time taken for the cloud to become inert is given by putting $x_i = (ut)$

DAMAGE TO STRUCTURES

The response of structures to dynamic loading by shock waves in air has been extensively studied for military purposes. The results are generally expressed as the damage to be expected from a shock of a specified peak over-pressure.

This is an approximation. Damage is dependent not only on the peak pressure but also on the time constant of the pressure decay and on the natural vibrational frequency of the structure. However, for practical purposes this may be ignored, and the following values be used

Pressure		Damage
psig.	kN/m^2	
0.03	0.2	Occasional breakage of glass windows
0.1	0.7	breakage of some small windows
0.3	2	probability of serious damage beyond this point = 0.05; 10% glass broken
0.4	3	minor structural damage to buildings
1.0	7	partial demolition of houses, uninhabitable; corrugated panels displaced
2.0	14	partial collapse of house walls and roofs
3.0	20	steel frame buildings distorted, pulled from foundations
4.0	28	oil storage tanks ruptured
5.0	35	wooden utilities poles snapped
6.0	42	nearly complete destruction of houses
7.0	50	loaded wagon trains overturned
10.0	70	total destruction of buildings; heavy machine tools moved and damaged; very heavy machine tools survived.

SYMBOLS USED

C = Sutton's diffusion constant (m.)

E = efficiency factor for TNT equivalent

F = quantity of vapour in combustible region (g)

n = Sutton's meteorological constant (dimensionless)

Q = total quantity of vapour in cloud (g)

r = radius (m)

t = time (sec.)

v = variance (m^2)

x = distance of centre of cloud from origin (m)

σ = standard deviation of concentration distribution (m)

σ_m = s.d. when cloud is at maximum potential (m)

χ = vapour concentration (g/m^2)

χ_o = vapour concentration at centre of cloud (g/m^2)

χ_r = vapour concentration at distance r from centre (g/m^2)

χ_u = upper flammable limit (g/m^2)

χ_l = lower flammable limit (g/m^2)

μ_n = n th. moment about the mean (m^n)

β_2 = kurtosis coefficient (dimensionless)

REFERENCES

(1) O. G. Sutton, 1953, Micrometeorology, McGraw Hill, London

(2) W. C. Brasie and D. W. Simpson, 1968, Loss Prevention Vol. 2, p.91-103, Am. Inst. Chem. Eng., New York

(3) A. L. Kuhl, M. M. Kamel and A. K. Oppenheim, 1973, 14th. Symposium on Combustion, p. 1201

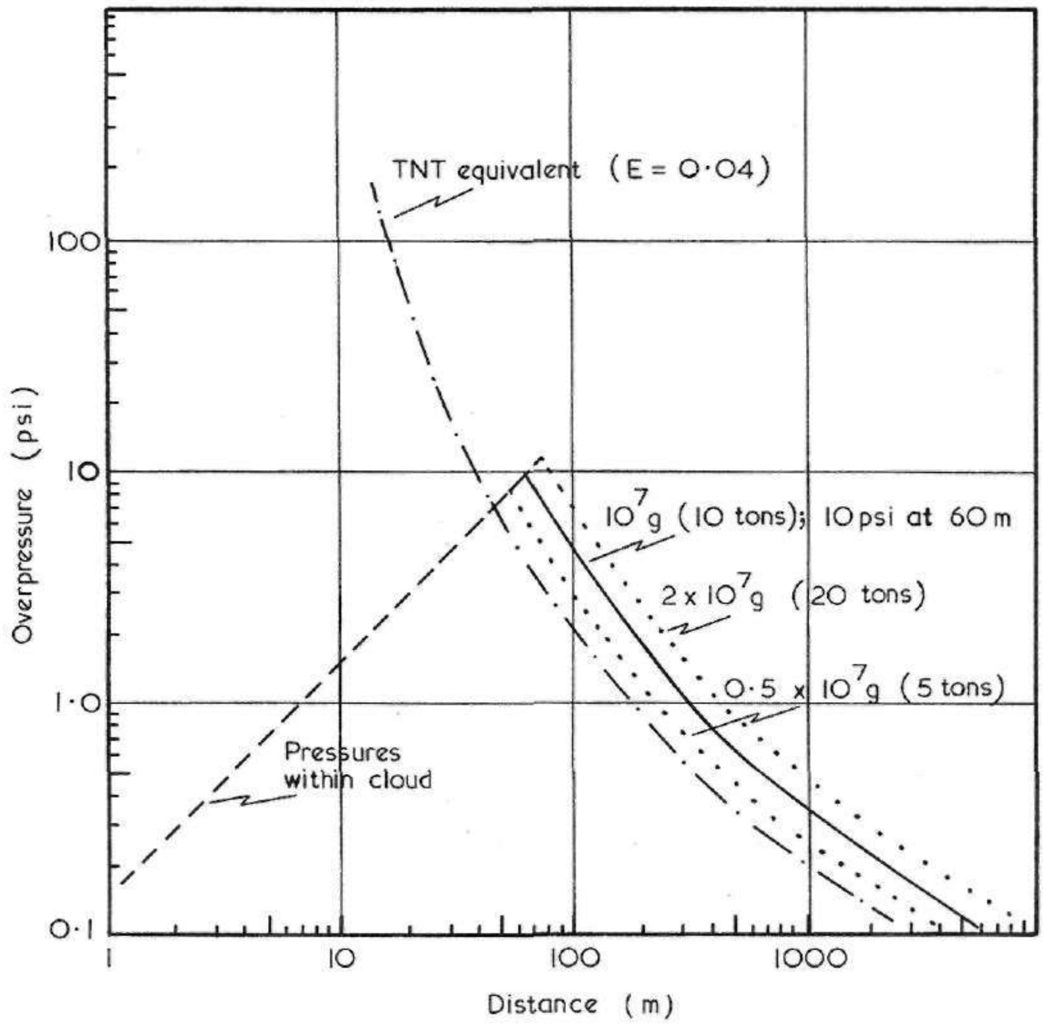

Fig. I Pressures from a propane cloud