

ATOMISATION AND DISPERSION OF TOXIC LIQUIDS RESULTING FROM ACCIDENTAL PRESSURISED RELEASES

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If hazardous liquids are released accidentally under pressure, a spray of liquid droplets may be produced. A model for dispersion and evaporation of droplets has been developed to calculate airborne concentrations and hazard ranges. A literature search was carried out to determine the state of the art for predicting spray droplet size distributions. In lieu of information on accidentally formed orifices, empirical correlations developed for engineered atomisers were recommended. Scoping calculations for three substances of interest were carried out, and the dependency of concentrations and hazard ranges on input assumptions was investigated. Atomisation remains the main source of uncertainty.

KEY WORDS: Droplet, Dispersion, Evaporation, Atomisation, Toxic

INTRODUCTION

Many hazardous substances exist as liquids under normal conditions and are transferred or stored under pressure. Under these circumstances, the accidental release of liquid through an orifice (which, for example, may be a split/crack or a flange) may well result in the formation of a liquid spray due to the break-up of an unstable liquid jet. The inhalable droplets formed by such a spray release may be small enough to be carried a significant distance downwind. While airborne the droplets will vaporise and gradually reduce in diameter, or possibly evaporate completely. The extent to which this occurs before droplets impinge on the ground depends upon amongst other things, the size of the droplets and the volatility of the liquid.

In performing a hazard analysis of a pure liquid release it is often convenient to consider just two extremes:

- all the liquid impinges on the ground forming a liquid pool, which subsequently evaporates;
- all the liquid remains airborne within a cloud, which then disperses in the atmosphere like the vapour.

Considering only these two extremes may however be quite unsatisfactory for certain low volatility, very toxic substances. Such substances may pose little hazard from an evaporating pool, but may give a significant hazard if all the droplets are assumed to remain airborne within the cloud. This appears to be the case for some of the very toxic chemicals which are included in the second amendment of the CIMAH Regulations. The present paper describes a pilot study

exploring how a more realistic assessment of the formation and subsequent fate of droplets might be carried out.

The study consisted of three parts:

- a literature review of the atomisation of liquid jets, to identify suitable methods for *estimating the droplet source term*;
- the development of a model of spray droplet dispersion and evaporation in a steady-state plume, treating: droplet fall-out as a function of size; droplet evaporation as a function of size; droplet advection as a function of height; vapour advection by the wind; and plume spreading due to atmospheric turbulence;
- example calculations using the models, for three liquids of interest: toluene di-isocyanate (TDI), di-methyl sulphate (DMS) and phenol.

ATOMISATION REVIEW

The complexity of the atomisation processes make analytical predictions of the droplet size distribution impracticable. It was decided in this study to use empirical correlations for the droplet size distribution. An extensive survey of the literature revealed no experimental studies of the type of sprays which would be produced by fractures and other orifices produced accidentally. The correlations for the droplet size distribution recommended below were obtained from studies of diesel injectors, and were chosen here in the absence of experimental results more relevant to the accident situation.

A spray can be characterised by a mean diameter. The general form of a mean diameter, d_{ab} , is, for a discretised distribution:

$$d_{ab} = [(\Sigma n_i d_i^a) / (\Sigma n_i d_i^b)]^{1/(a-b)} , \quad (1)$$

where Σ indicates the sum over all size classes i with class diameter d_i , and n_i is the number of droplets in class i . It is common to describe a spray using the Sauter Mean Diameter (SMD), d_{32} . As a result of the review it was recommended that the SMD of sprays be estimated using the dimensional correlation proposed by Elkoth (1):

$$d_{32} = 3.09 \nu^{0.385} (\sigma\rho)^{0.737} \rho_g^{0.06} \Delta P^{-0.54} , \quad (2)$$

where ν , σ and ρ are the liquid kinematic viscosity, surface tension and density respectively, ρ_g is the gas density and ΔP is the pressure drop across the orifice. The distribution recommended was the chi-squared form which Hiroyasu and Katoda (2) fitted to their data. The fraction of the total liquid volume in particles with diameters between d and $d+\Delta d$ is:

$$\Delta V/V = 13.5 \phi^3 e^{-3\phi} \Delta \phi , \quad (3)$$

where $\phi = d/d_{32}$.

Elkoth tried a number of distribution types and also concluded that the chi-squared distribution gave the best fit. His distribution:

$$\Delta V/V = 1953 \phi^{7.5} e^{-7.5\phi} \Delta\phi, \quad (4)$$

can be used for sensitivity tests.

DISPERSION AND EVAPORATION MODELLING

The dispersion model starts with a point source of droplets at a given point moving horizontally with the local wind velocity and vertically downwards each with its terminal velocity. In this model the spatial extent and initial momentum of the spray have been ignored. The model represents the size distribution by a set of discrete size classes, each characterised by a class diameter d_i , and associated with a total mass m_i of liquid in the class. A representative droplet from each class is followed using three differential equations, corresponding to:

- (a) the falling of the droplet under gravity ;
- (b) the translation of the droplet down-wind;
- (c) the evaporation of the droplet.

These three equations are coupled. The rate at which the droplet falls is given by its mass, and the rate at which it loses mass by evaporation depends on its velocity relative to the surrounding gas. The horizontal velocity is given by the local wind speed, which is a function of height. The three processes are now discussed in more detail.

Droplet Fall

There is a wide variety of correlations available for the terminal velocity of droplets. In this study we used the formulae from Giffen and Muraszew (3):

laminar flow ($0 < Re < 2$) :

$$v = g \cdot d^2 \cdot (\rho - \rho_g) / 18 \eta_g ; \quad (5)$$

semi-turbulent flow ($2 < Re < 500$) :

$$v = (2500 \eta_g^2 / \rho_g^2 \cdot d^2 + g \cdot d(\rho - \rho_g) / 0.3 \rho_g)^{1/2} - 50 \eta_g / \rho_g \cdot d ; \quad (6)$$

turbulent flow ($500 < Re < 10^5$) :

$$v = (g \cdot d(\rho - \rho_g) / 0.33 \rho_g)^{1/2} \quad (7)$$

Here η_g is the gas dynamic viscosity and g is the acceleration due to gravity. The Reynolds number, which determines the flow regime, is given by

$$Re = (\rho_g v d) / \eta_g \quad (8)$$

Droplet Advection

The model has wind velocity profiles for Pasquill classes B, D and F (Businger *et al* (4)). The representative wind speeds at 10 m have been taken as 2, 5 and 2 m/s respectively. The roughness length z_0 and von Karman constant k_a have been taken to be 0.01 m and 0.4 respectively in all cases. The friction velocity u_* has been chosen to give the required speed at height 10 m, and the Monin-Obukhov length L is 9.53 m for class F and -10.54 m for class B. The wind velocities u_z as functions of height z , are

Class D (neutral)

$$u = u_* \ln(z / z_0) / k_a \quad (9)$$

where $u_* = 0.28953$ m/s

Class F (stable)

$$u = u_* (\ln(z/z_0) + 4.7 z/L) / k_a \quad (10)$$

where $u_* = 0.06757$ m/s

Case B (unstable)

$$u = u_* [\ln(z/z_0) - \ln((1+x^2)/2) - 2 \ln((1+x)/2) + 2 \tan^{-1}x - \pi/2] / k_a \quad (11)$$

where $u_* = 0.13677$ m/s, and $x = (1-15z/L)^{1/4}$

Droplet Evaporation

The equation used in the model for the rate of mass lost by the diffusive flux of vapour from an evaporating droplet is (see Davies and Shaw (5) and Kukkonen *et al* (6)):

$$dm/dt = -2\pi d \text{ Sh } M_v D (p/T - p_\infty/T_\infty) / R \quad (12)$$

where

m	mass of drop
d	diameter of drop
M_v	molecular weight of the material of the drop
D	diffusion coefficient of the vapour in air
p	pressure of vapour at the drop surface
p_∞	pressure of vapour away from the drop
R	gas constant
T_d	Temperature of the drop
T_∞	Temperature of the atmosphere

and the Sherwood number, Sh , depends on the terminal velocity of the drop via the correlation:

$$Sh = 1 + 0.276 * Re^{1/2} * Sc^{1/3} . \quad (13)$$

Here Sc is the Schmidt number, $\eta_g/(\rho_g D)$

In the initial stages of this study it was proposed to ignore the effect of background pressure of vapour, p_∞ , the assumption being that it would be negligible. However this assumption proved to be not valid at least near the source of the drops. An iterative procedure was needed, each iteration taking the vapour concentrations from the previous one. Some smoothing of the concentration changes was needed to avoid large oscillations. In the study ten iterations were used, and the results at the end points were found to be successfully converged.

Separate calculations were made of the temperature of the droplets and it was found that, to a good approximation, the ambient temperature could be used. This however would not be the case for more volatile substances.

Concentration Calculations

For each representative droplet the model is used to determine, for a given vertical plane normal to the wind direction some distance downwind, whether it:

- (i) crosses the plane, or
- (ii) falls to the ground before crossing the plane, or
- (iii) evaporates completely before crossing the plane.

The number of droplet classes crossing the plane is converted into a mass flow of liquid across the plane. Similarly information on how much vapour has been created upwind of the plane is converted into a vapour flow rate across the plane.

Given the mass flux $W(x)$, either of liquid or vapour, at some downwind distance x , then the concentration (mass per unit volume) there is approximated by

$$C(x) = W(x) / \Delta z(x) \Delta y(x) \langle u \rangle . \quad (14)$$

The cross-wind extent of the cloud, $\Delta y(x)$, is calculated from the cross-wind spreading rates used in Gaussian plume models (Panofsky and Dutton (7)). The vertical extent of the cloud, $\Delta z(x)$, is first calculated by taking the distance between the uppermost and the lowermost particle trajectory (this is for the particles; for the vapour the uppermost trajectory is replaced by the height of release). The velocity $\langle u \rangle$ is the wind velocity averaged over the vertical extent of the cloud. This extent is then corrected to take account of vertical spreading, as given by the Gaussian plume models. This spreading correction is the only account taken in the model of the effects of turbulence on the cloud.

RESULTS

The physical properties required by the model were taken, for the three liquids of interest, from the DIPPR database (8), apart from the diffusivities, which were calculated using the methods of Reid, Prausnitz and Poling (9). A calculation matrix was made up of the three liquids, the three weather classes and three release conditions:

Example 1: Guillotine break

Here we consider the case where the pipe is severed leading to a circular orifice of diameter given by the internal pipe diameter.

Release rate	3 kg/s
Pipe diameter	0.015 m
Height of pipe	1 m

Example 2: Circumferential leak from a pipe

Here we consider the release of liquid through a narrow gap around the circumference of a pipe. The release is considered to occur only through the top half of the circumference.

Release rate	0.3 kg/s
Pipe diameter	0.15 m
Gap width	50×10^{-6} m
Height of pipe	1 m

Example 3: Elevated release

In this case an elevated release under the same conditions as example 2 is considered.

Release rate	0.3 kg/s
Pipe diameter	0.15 m
Gap width	50×10^{-6} m
Height of pipe	10 m

These cases were specified as described here as useful inputs to test the model. They do not necessarily represent specific initial accident conditions. (A simple release rate model was used calculate from these data a release pressure, needed for the atomisation correlations.)

These three break types, taken together with the three substances of interest, and the three weather conditions gives us a matrix of 27 separate cases. In this study calculations were performed for 16 of these cases. The results of these calculations are summarised below in table 1 (this shows the full matrix of cases, with cases not calculated left blank). Each calculation is given an arbitrary "run number" (runs 1 and 14 are variants of runs 2 and 10 respectively and, run 19 is a variant on run 15, as explained below.) The information given is the concentration at 100 and 1000 m (with the letter "d" indicating that there are still drops airborne), the distance at which the last droplets fall out, and the hazard range. To define a hazard range we take a dangerous toxic load as 200 ppm.min, and therefore a dangerous concentration as being 20 ppm,

corresponding to a notional 10 min exposure. The hazard range is the point at which the concentration drops below this value. (This choice of toxic load value will be grossly pessimistic for phenol, which has a significantly lower toxicity than TDI and DMS).

The main result of the calculations is that, for the atomiser correlations used, almost all the liquid (around 99%) impinges on the ground before it has a chance to evaporate. Only droplets from a few of the smallest size classes evaporate completely while airborne. Given this result, the hazard arising from evaporation from the liquid pool which may be formed by such a spray could be more significant than the vapour plume formed by the evaporation of the airborne droplets. However, the fate of the material on the ground is outside the scope of the current study. The more detailed effects to be seen on table 1 are the following.

Effect of Material

By comparing runs 2 and 3, and runs 11 and 12 we see that, for the same circumstances, the concentrations are highest for DMS and lowest for TDI, with phenol concentrations lying in between. This is to be expected on the basis of the differing volatilities.

Effect of Break Type and Height

The main effect is that of height, as can be seen by comparing the results from break types 2 and 3 with material and weather kept constant. The hazard ranges and most of the concentrations are greater for the more elevated release, which allows the droplets to be carried downstream for a longer time. Comparing the guillotine break (type 1) with the circumferential leak (type 2) but everything else unchanged shows that the former gives the higher concentrations, because of the higher leak rate from the guillotine break.

Effect of Droplet Size Distribution

Comparing run 1 with run 2 and run 14 with run 10 shows the effect of shifting from the Hiroyasu/Katoda to the Elktob distribution. This is because the former correlation gives more small particles than the latter.

In some cases the Sauter mean diameter of the droplets predicted by the correlation used was greater than the smallest dimension of the orifice producing the droplets. This was felt to be physically unrealistic, and was taken as evidence that the correlation was being used outside the pressure-drop range for which it is valid. As a sensitivity study, run 19 was performed, which repeated run 15 but with an upper cutoff of 50 μm on the Sauter Mean Diameter for the initial droplet distribution. This increases the concentration at 100 m by a factor of 50, that at 1 km by a factor of 10, and shifts the hazard range from 120 to 500 m. This demonstrates the importance of obtaining better information on droplet formation with orifices relevant to safety studies.

TABLE 1 - SUMMARY OF RESULTS

	weather	case	run	conc/ppm		distance to last droplets/m	hazard range /m
				100 m	1000 m		
phenol	B	1	(7)	0.08	0.0001	20	< 20
		2	(2)	0.08	0.00004	20	< 20
		2	(1)*	0.01	0.00002	20	< 20
		3	(9)	3.0 (d)	0.0003	180	80
	D	1					
		2	(5)	0.07	0.0003	60	20
		3	(10)	90 (d)	0.001	440	160
		3	(14)*	20 (d)	0.0006	460	100
	F	1					
		2	(6)	1.0	0.005	< 20	20
		3	(11)	10 (d)	0.002	140	60
DMS	B	1					
		2	(4)	0.05	0.00006	< 20	20
		3	(18)	0.09	0.0003	80	60
	D	1					
		2					
		3	(13)	20 (d)	0.002	180	95
	F	1					
		2					
		3	(12)	0.08	0.003	60	40

TABLE 1 - SUMMARY OF RESULTS (CONTINUED)

	weather	case	run	conc/ppm		distance to last droplets/m	hazard range /m
				100 m	1000 m		
TDI	B	1	(8)	0.004	0.000005	20	20
		2	(3)	0.001	0.000002	20	< 20
		3	(17)	5.0 (d)	0.00001	460	80
	D	1					
		2					
		3	(15)	40 (d)	0.001 (d)	> 1000	120
		3	(19) [†]	2000 (d)	0.01 (d)	> 1000	500
	F	1					
		2					
		3	(16)	1.0 (d)	0.0001	420	50

* Runs 1 and 14 are variants with the Elktob rather than the Hiroyasu/Katoda distribution

† Run 19 implements a cutoff of 50 μ m on the Sauter Mean Diameter for the initial drople distribution.

Effect of Weather Conditions

In runs 2, 5 and 6 (1 m high releases of phenol) we see that at a distance of 1 km the highest concentration is given by the stable conditions (category F), and the lowest by unstable condition (category B). Category D, the neutral condition gives a result in between. This is the order expected for vapour releases. The dependence on weather is strong, with about an order of magnitude difference between the concentration in each category. However all these concentrations are well below the danger level of 20 ppm, the highest value being only 0.005 ppm. If we look at a location where concentrations are around the danger level, namely 100 m from a 10 m high phenol release (runs 9, 10 and 11), the pattern is different. Here the weather conditions determine whether or no the concentration is above the danger level at 100 m, with neutral stability giving the highest value

To show this effect in more detail, some of the results from these runs are reproduced below on table 2. How far the droplets travel before they fall out depends on the competition between their fall velocity and their horizontal velocity, given by the wind speed corresponding to their height. The dependency of the 100m concentration on weather is an effect of wind-speeds, which vary from

one category to the other. For example the wind speeds at the 1 m height are 1.5, 3.3 and 0.9 m/s for categories B, D and F respectively. At 1km the pattern expected from vapour dispersion is re-established. By this distance the remaining airborne phenol is all vapour.

Table 2. The Effect of Weather Conditions on the Phenol Release at 10 m

Stability	Run Number	Conc. at 100m (ppm)	Conc. at 1 km (ppm)	Distance to Last Drop (m)
unstable	9	3	0.0003	180
neutral	10	90	0.0010	440
stable	11	10	0.0020	140

The evaporation rate of the droplets will increase with increasing ambient temperature. In this study the overall effect of varying the temperature has not been explored; all the calculations have been done with an ambient temperature of 17°C. The choice of this comparatively warm day is conservative.

CONCLUSIONS

A model has been developed for the dispersion and evaporation of droplets formed when liquids are sprayed out of accidentally formed orifices under pressure. It incorporates the following features:

- droplet fall-out as a function of size;
- droplet evaporation as a function of size;
- droplet advection with the windspeed as a function of height;
- vapour advection with the wind;
- plume spreading due to atmospheric turbulence.

If necessary the model can be iterated to take account for the suppression of evaporation due to the presence of the surrounding vapour. The model takes as input the contaminant flow rate, initial droplet size distribution, the height of the release, and the atmospheric conditions, as characterised by a stability class and wind speed profile.

A literature survey was carried out to determine the characteristics of a spray release resulting from the loss of containment of a pressurised liquid. The processes involved in atomisation are generally regarded as being too complex for mathematical analysis. Because of the lack of data on atomisation by fractures, empirical correlations for engineered atomisers have been used to provide input to the dispersion calculations. Correlations based on engineered atomisers are likely

to be pessimistic, in that such atomisers are engineered to most efficiently mix the released liquid into the receiving medium, whereas most release orifices for accidental discharges will not be. However, it should be noted that for the relatively low pressure releases of interest (typically a few bar gauge for hazardous liquid transfer) through possibly irregular orifices, these correlations are essentially unvalidated. Further experimental studies are required in order to provide measurements of appropriate spray quantities under these conditions and with more appropriate orifice geometries.

Scoping calculations for phenol, dimethyl sulphate and toluene di-isocyanate have been performed. These calculations illustrate some of the key factors influencing downwind concentrations and hazard ranges. Changes in the height of release, weather category and droplet size distribution can cause order-of-magnitude changes in concentrations and ranges. In particular, imposing on the atomisation correlations the additional constraint that droplets should not be larger than the orifice increases concentrations and hazard ranges significantly. With the atomiser correlations used, almost all the liquid (around 99%) is predicted to impinge on the ground before it has a chance to evaporate. Only droplets from a few of the smallest size classes evaporate completely while airborne. Given this result, the hazard arising from evaporation from the liquid pool which may be formed by such a spray, could be more significant than the vapour plume formed by the evaporation of the airborne droplets. However, the fate of the material on the ground is outside the scope of the current study.

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