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Liquid dispersal and vapour production during overfilling incidents

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Physical processes

Liquid flow

The nature of the liquid release from an overfilled tank depends primarily on the flow rate and on the tank design. Three categories of tank have been identified that differ significantly in the character of the liquid release in the event of overfilling:

Type A: Fixed roof tanks with open vents (typically with an internal floating deck);

Type B: Floating deck tanks with no fixed roof;

Type C: Fixed roof tanks with pressure/vacuum valves and possibly other larger bore relief hatches.

Liquid release from type A tanks

This is the type of tank that was involved in the Buncefield incident. This tank was typical of type A tanks with a number of open breather vents close to the edge of the tank at a spacing of around 10 m around the perimeter.

Tanks of this sort may be provided with a fixed water deluge system, which delivers water to the apex of the conical top of the tank. In the event of a fire, injected water flows down over the tank roof. Typically there is a 'deflector plate' at the edge of the tank, which redirects water draining from the top of the tank onto the vertical tank wall.

In the event of tank overfilling, liquid will flow out of the open vents, spreading a little before it reaches the tank edge. The flow rates during overfilling are typically much higher than cooling water flow for which the deflector is designed. A proportion of the liquid release is directed back on to the wall of the tank and a proportion simply flows over the edge of the plate. This is illustrated in Figure 1.

Some tanks, including the tank involved in the Buncefield incident, have wind girders part way down the tank wall to stiffen the structure. Any liquid falling close to the tank wall will hit this girder and be deflected outwards, away from the tank wall. This outward spray may intersect the cascade of liquid from the top of the tank. This is illustrated in Figure 2.

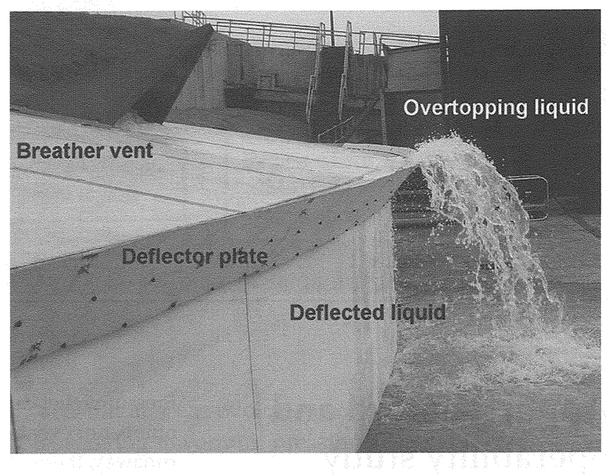


FIGURE 1: LIQUID RELEASE FROM A VENTED FIXED ROOF TANK WITH A DEFLECTOR PLATE

FIGURE 2: INTERSECTION OF FREE CASCADES FROM A TYPE A TANK WITH A DEFLECTOR PLATE

The lateral spread around the tank perimeter of the free cascade of liquid formed from each breather vent is slightly greater if a deflector plate or wind girder is present. With these features present, the spray typically extends approximately 3 m around the tank perimeter. If the vents are spaced at 10 m intervals and the elevation of the vents is similar, the final result is a series of liquid cascades that cover approximately 30% of the total tank perimeter.

Liquid release from type B tanks

Floating deck tanks with no fixed roof typically have a large wind girder close to the top of the tank wall. This is fully welded to the side of the tank (to avoid stress concentration) and may be used as an access way (Figure 3). Small bore holes drain the top girder shelf but in the event of an overfill almost all the liquid overtopping the wall of the tank will flow out over the edge of the top girder forming a cascade. Typically the top girder is wide enough that liquid will not subsequently contact the tank wall and will therefore form a free cascade.

The proportion of the tank perimeter over which this cascade extends is likely to depend on the construction of the tank. Any variations in the elevation of the tank wall will tend to concentrate the release on one side of the tank. Similarly any damage to the tank wall by the floating deck or access to this deck prior to the overflow may concentrate the release in an even smaller fraction of the tank perimeter. It is unlikely to extend round the full tank perimeter.

Liquid release from type C tanks

Pressure/vacuum valves provided for pressure balancing during filling and emptying operations will generally not be adequate to relieve the liquid flow during overfilling. Liquid will come out of larger bore pressure relief hatches if these are fitted or from a split in the tank if they are not. Normally the tank construction should ensure that any split is at the junction between the tank top and wall.

In any case, it is likely that the release will be concentrated in a cascade covering a relatively small proportion of the total tank perimeter.

FIGURE 3: TOP GRIDER (WALKWAY) IN FLOATING ROOF TANK

Liquid dispersal

There do not appear to have been any previous studies of high volume, low momentum liquid releases that accelerate and disperse under the action of gravity. Some large-scale tests on water and petrol undertaken in the aftermath of the Buncefield incident have provided some useful indicators but there is a pressing need for more data.

In the first few metres of fall the large scale liquid strings and lamellae formed in the release separate and accelerate, dividing into large droplets with a diameter of approximately 10 mm. The fate of these large fragments depends on the mass flux density of liquid in the cascade (i.e. the amount of liquid falling through each square metre per second). If the flux density is relatively low most of the initial liquid fragments rapidly shatter to form a range of secondary droplets a few millimetres in diameter. The characteristic size is clearly a function of the liquid surface tension. Comparisons between 15 m high water and petrol cascades at similar mass densities showed that, at ground level, the droplets of water are variable in size in the range 2–5 mm whereas the characteristic size of petrol droplets are around 2 mm.

If the liquid flux density is very high, the aerodynamic drag forces on individual droplets in the core of the cascade will be lowered and some of the large fragments initially formed may persist for the full height of the drop.

All of the droplets then hit the ground. In cascades with high liquid mass flux densities the droplet impact speed may considerably exceed the terminal velocity for a single drop. Again the number and size of smaller secondary droplets formed on impact depends on the surface tension, impact speed and the nature of the impact surface i.e. wetted solid or deep liquid.

An initial estimate of the size range of secondary droplets produced by a petrol cascade impinging onto a bund floor can be made using the droplet splashing model of Bai et al.[5] This predicts secondary droplets of diameter 130–200 microns for impingement on a dry floor and 100–180 microns diameter for a wetted floor. The total mass of splash products is very dependent of the depth of liquid on the impact surface and may even exceed the incident droplet mass in some circumstances.

In this paper, the phrase 'vapour flow' is used to describe the air drawn into a liquid cascade and any gas produced from the liquid evaporating and mixing with the air. The fineness of droplets in the splash zone is very significant because the vapour flow driven by the cascade (described in the next section) passes through the splash zone. There is an opportunity for very rapid exchange of mass, heat and momentum. Exchanges of heat and mass in the splash zone drive the liquid and vapour flows closer to thermodynamic equilibrium. Fine (100–200 micron diameter) droplets rapidly picked up by the vapour flow in the splash zone absorb momentum from the vapour flow and this may have a significant effect on its subsequent dispersion.

It is worth pointing out that the settling velocity for droplets in the size range 100–200 microns is 0.2 to 0.8 m/s. This means that droplets this size may remain airborne for approximately 1–5 seconds during which they may be convected a distance of approximately 10 metres from the base of the tank. This means that some liquid droplets may remain suspended in the vapour flow as it impacts on the bund wall or other tanks within the bund.

Air entrainment

Jets of air or buoyant plumes entrain air through the action of shear driven vortices. A dense liquid cascade entrains air in a different, somewhat less complex way. Individual falling drops drag the air within the cascade downwards and air is drawn in through the sides to compensate. There are shear forces and induced vortices at the edge of the cascade but if the cross section is large these processes make little difference to the total volume flux of air — which is the quantity of primary interest.

A comparison has been made of detailed CFD predictions, which have included all the aerodynamic processes involved in falling sprays, and a simple momentum conservation model which ignores the induced shear flow on the spray periphery. This has shown that for the scenarios considered here it is adequate to use the latter, simpler treatment, which is described in Annex 1. Typical results obtained using the simple momentum conservation model are shown in Figure 4. In overfilling incidents the mass flux density is likely to be in the range 1 to 10 kg/m^2/s. This corresponds to maximum droplet velocities of 10–13 m/s and vapour velocities of 4–6 m/s.

CFD methods are capable of calculating droplet and vapour velocities both in the liquid cascade and in the vapour flow spreading out from the foot of the tank. These calculations fully encompass exchange of mass, heat and momentum between liquid and vapour phases.

Vaporisation of liquid

The fineness of liquid dispersal controls the extent to which liquid and vapour approach thermodynamic equilibrium. Example results from a CFD study of heat and mass transfer in the cascade are shown in Figure 5.

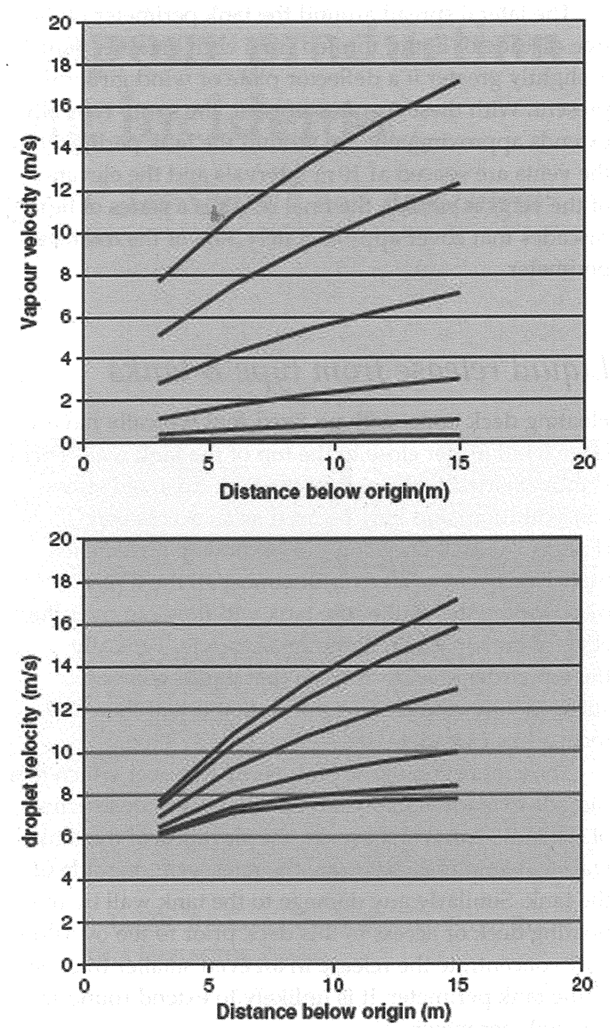


FIGURE 4: VAPOUR AND DROPLET VELOCITIES INDUCED BY LIQUID CASCADES OF DIFFERENT DENSITIES. THE HIGHEST VELOCITIES SHOWN IN BOTH PLOTS (FOR COMPARISON) CORRESPOND TO FREE-FALL WITH NO AIR RESISTANCE. THE LOWER VELOCITIES CORRESPOND RESPECTIVELY TO LIQUID FLUX DENSITIES OF 100, 10, 1, 0.1 AND 0.01 KG/M^2/S

For droplets of a diameter of 2 mm or less, droplets and vapour in the core of the cascade (where the mass flux is concentrated) are very close to equilibrium. Areas on the fringes of the cascade where there is a greater proportion of fresh air are clearly further from equilibrium.

The CFD modelling shown in Figure 5 does not include droplet splashing — droplets in the model disappear on impact with the ground. The presence of the pool of liquid in the bund around the base of the tank is also ignored. It is likely that in most circumstances the splash zone at the base of the tank is an additional area where vapour and very finely divided liquid are vigorously mixed for a significant period of time, which pushes the whole of the flow closer to equilibrium.

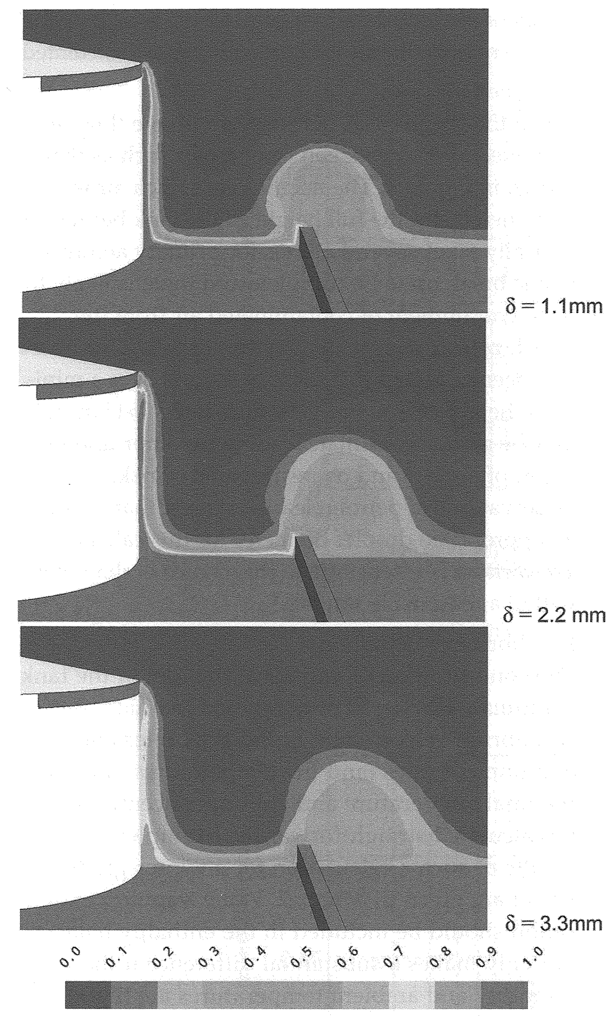


FIGURE 5: CONTOURS OF THE RATIO OF PREDICTED VAPOUR VOLUME FRACTION TO THE SATURATION VOLUME FRACTION. A VALUE OF 1.0 INDICATES THAT THE VAPOUR IS SATURATED. THE THREE PREDICTIONS ARE FOR DIFFERENT INITIAL DROPLET SIZE DISTRIBUTIONS USING THE ROSIN-RAMMLER DIAMETERS SHOWN

In the scoping method described in the next section it is assumed that the liquid released and the gas flow that it entrains in the cascade and splash zone are in thermodynamic equilibrium. This is a conservative assumption in the assessment of vapour cloud production but available information on liquid dispersal and heat and mass transfer calculations suggest it is also reasonably close to the truth in most cases.

One important exception to this may be tanks where high volume releases are concentrated in very small sections of the tank perimeter. Releases from many type C tanks could be of this sort. Very high liquid mass flux densities (100 kg/m^2/s) could result. In this case liquid dispersal would be limited and the spray would be composed of very large droplets or streams of liquid. For the very large liquid fragments, the rate of vaporisation could be limited by the ability of lighter, more volatile fractions to diffuse to the surface of the liquid in contact with the air. This is significant in the analysis of the potential for type C tanks to produce flammable clouds when overfilled with liquids composed of only a small volume fraction of volatile material e.g. light crude oils.

Near field dispersion

Generally, dispersion of a release of flammable vapour cloud is treated separately from the source term (unless a full CFD treatment of the whole release is possible). To take this approach it is necessary to identify where the source term ends and the dispersion calculation should begin. The choice taken here for this point of separation is at the base of the tank or at the edge of the zone where the vapour flow is deflected into the horizontal.

Care has to be taken in joining source term and dispersion calculations in this way. High vapour velocities (5 m/s) are typically induced by the cascade at the foot of the tank. Even though the flow is denser than air, such a flow will entrain air as it flows out across the floor of the bund. This entrainment process occurs whether the flow impacts on a bund wall (as in Figure 5) or not. Any entrainment of fresh air after the bulk of the liquid has rained out will result in a reduction in vapour concentration. Contact between the vapour and liquid pool on the floor of the bund may on the other hand increase the concentrations, although this may be limited since the vapour close to the floor of the bund may be close to being saturated already.

There is a tendency for the entrained air to move through the cascade towards the tank wall (the Coanda effect). This means that the bulk of the vapour flow passes through the droplet splash zone at the base of the tank (see Figure 6). Droplet splash products are capable

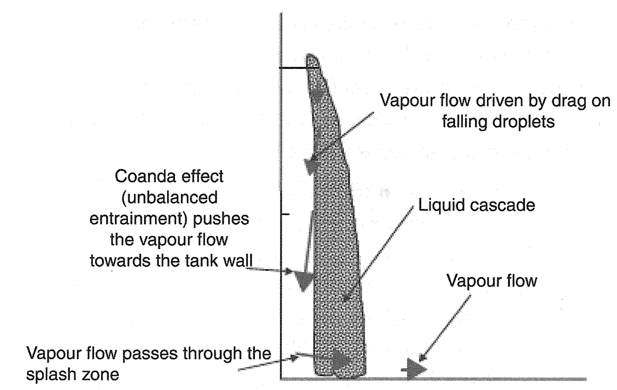


FIGURE 6: SCHEMATIC SHOWING VAPOUR FLOW DRIVEN BY A FREE LIQUID CASCADE

of absorbing part of the vapour jet momentum and consequently suppressing the tendency for entrainment—even in the near-field. This effect is still under investigation. Large-scale experimental releases of hydrocarbons are needed to obtain reliable data on the flow behaviour for this case.

Scoping method

Approach and assumptions

The scoping method described here is based on the principle that production of vapour concentrations within the flammable range at the base of the tank will bring liquids 'in scope'. This is a somewhat conservative, but reasonable, assumption that might be refined if more was known about the splashing process and its effects of the near-field dispersion.

The method provides a means of determining whether a given filling operation in a given tank can lead to the generation of a flammable cloud. Such a scoping method is clearly of interest in determining the appropriate level of protection against overfilling. The volume and concentration of flammable vapour close to the source are outputs but to predict the potential extent of the cloud would require a dispersion model.

Although it may appear initially counter-intuitive, the likelihood of producing flammable vapour for many substances increases as the amount of fresh air entrainment is reduced. Enhanced air entrainment leads overall to greater evaporation but the vapour produced is often below the lower flammability limit.

The scoping method is divided into a number of stages which are described below:

1. Proportion of tank perimeter covered by liquid release
   It is assumed that in all cases the liquid released is distributed over 30% of the tank perimeter. In the case of type C tanks this may be an overestimate. In principle this might lead to a non-conservative overestimation of the induced vapour flow, however this is unlikely to lead to serious underestimates of risk because of the relatively low sensitivity of the induced flow to the liquid mass flux and the tendency for vapour concentrations to fall short of equilibrium at very high liquid mass fluxes.
2. Liquid mass flux in the cascade
   The distance the spray extends away from the tank wall is assumed to be 1.5 m over the full height of the cascade. This is a reasonable minimum figure based on observations on water cascades. Wind girders part way down the tank can increase the width to in excess of 3 m but any broadening of the liquid cascade increases the total induced air flow and tends to reduce the maximum vapour concentration. Given the cross section of the cascade and the total liquid release rate the liquid mass density can be calculated.
3. Entrained air flow
   Given the liquid mass density the volume flow of entrained air can be taken from a plot such as that shown in Figure 4. The height over which air is entrained is not the full height of the tank because it typically takes several metres for primary aerodynamic break up to be complete and there is likely to be re-entrainment of contaminated air from the splash zone in the last few metres of fall. It has therefore been assumed that air is entrained over a minimum height of 6 m. For very high tanks (>15 m) this may be an underestimate leading to minor underestimates of airflow and overestimation of risk. Observations of petrol releases suggest that 2 mm is an appropriate droplet diameter for this calculation. The airflow is insensitive to this choice of diameter within a reasonable range.
4. Equilibrium calculations
   The concentration of vapour at the foot of the tank is estimated by assuming thermodynamic equilibrium. Given total liquid flow rates and air entrainment rates (and the temperatures of both) the final temperature and vapour concentration can be calculated straightforwardly. Examples of results of such a calculation for a winter-grade petrol are given in Annex 2. Water vapour condensation should be included in the enthalpy balance but only makes a substantial difference if the humidity and ambient temperatures are high.
5. Comparison with flammability limits
   If the vapour concentration calculated in 4 exceeds the Lower Flammable Limit it is possible that overfilling of the tank will produce a flammable cloud.
   The method described above accounts for the fact that the temperature drop due to evaporation of spray droplets may reduce the saturation vapour pressure sufficiently to avoid the production of flammable vapour. This means that in some cases a substance that is flammable at room temperature, such as toluene, may not produce flammable vapour in the cascade from a tank overfilling release. In reality, in such cases, the liquid from the tank overfill will accumulate within the bund and may eventually rise to ambient temperatures and start to produce flammable vapour. This hazard could be modelled using standard pool-evaporation models.
   Results of such scoping analyses on typical high volume refinery liquids and crude oils are shown in Figures 7 and 8. Composition data for the mixtures analysed are shown in Annex 3. In all cases the temperature of the released fluid was 15°C and the ambient temperature 15°C. The independent variable is the total liquid release rate divided by the total tank diameter.

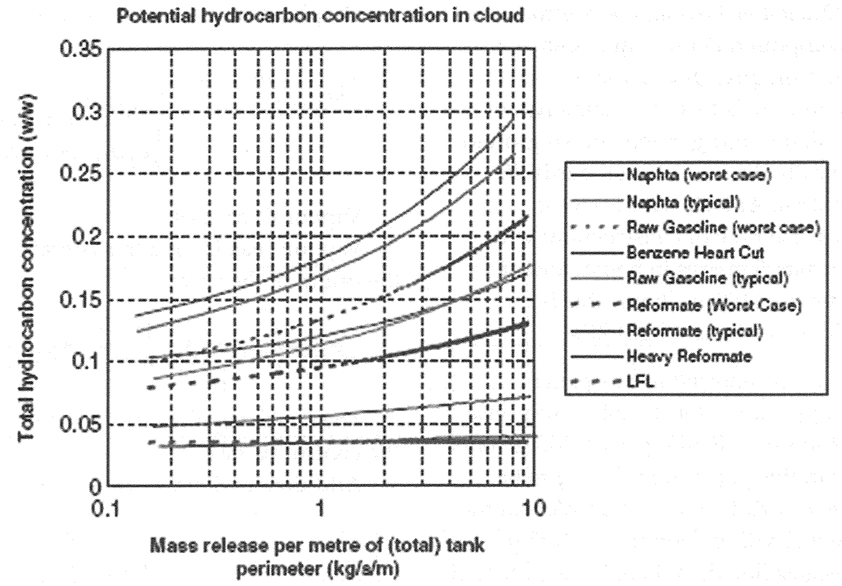


FIGURE 7: VAPOUR CONCENTRATIONS IN AIR DRIVEN BY CASCADES OF VARIOUS REFINERY LIQUIDS

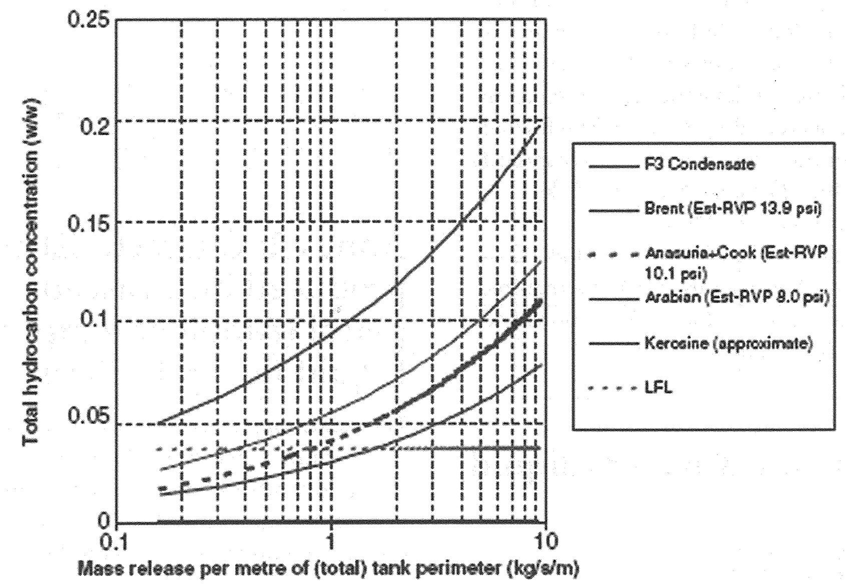


FIGURE 8: VAPOUR CONCENTRATIONS IN AIR DRIVEN BY CASCADES OF VARIOUS CRUDE OILS

Implications for safety and environmental standards at fuel storage sites

The technical work described in this paper was carried out in support of the Buncefield Standards Task Group (BSTG). The BSTG was formed soon after the Buncefield incident and consisted of representatives from industry and the joint Competent Authority for the Control of Major Accident Hazards (COMAH). The aim of the task group was to translate the lessons from the incident into effective and practical guidance.

To ensure focussed and timely responses to the issues arising from Buncefield the scope of application for the work of the task group was defined in the initial report by BSTG.[6] This was confirmed in the final report of July 2007[7] and is repeated here:

- COMAH top- and lower-tier sites, storing
- Gasoline (petrol) as defined in Directive 94/63/EC [European Parliament and Council Directive

94/63/EC of 20 December 1994 on the control of volatile organic compound (VOC) emissions resulting from the storage of petrol and its distribution from terminals to service stations], in

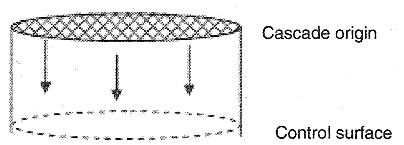
- vertical, cylindrical, non-refrigerated, above-ground storage tanks typically designed to standards BS 2654, BS EN 1401:2004, API 620, API 6508 (or equivalent codes at the time of construction) with
- side walls greater than 5 metres in height and at
- filling rates greater than 100 m^3/hour (this is approximately 75 tonnes/hour of gasoline).

The results of the work reported in this paper confirm the scope of application for the initial response to Buncefield. That is to say that all types of storage tank described previously in this paper are believed to be capable of generating a cascade of liquid droplets in the event of overfilling with hydrocarbon liquid. If that liquid hydrocarbon is gasoline then there is the potential for the formation of a large flammable vapour cloud.

This work also indicates that there is the potential for other substances with similar physical properties to behave in a similar way in the event of a loss of primary containment following overfilling. Work continues in order to establish an agreed definition for the extension of scope to a limited number of other substances. This might also lead to a better understanding of the release conditions that might lead to this scenario. The further work continues under the Petroleum Process Standards Leadership Group which has been formed to take forward the work started by the BSTG.

In the meantime the results of the work of BSTG have been taken forward as a series of actions required of operators. The final report[7] details these actions and includes the supporting guidance.

Annex 1: Gas flow driven by liquid cascade



Assume

1. The spray has little initial non-axial velocity and the cross section remains constant.
2. The spray is uniform over a given area with a mass flux density of M (kg/m2/s).
3. The induced gas phase velocity is constant across the section. The additional gas mass flow required is presumed to be entrained through the vertical boundary of the spray and rapidly mixed across the section.
4. The spray is monodisperse (i.e. all droplets are the same size).

Droplet dynamics

$$m_{droplet}\frac{du_{droplet}}{dt}=m_{droplet}\cdot g-\frac{1}{2}c_d\,\rho_{vap}\,A_{drop}(u_{droplet}-u_{vapour})^2$$

Vapour dynamics

Vapour velocity at a horizontal control surface below the origin of the spray

$$\rho_{vap}u_{vapour}^2=\sum_{droplets}\frac{1}{2}c_d\,\rho_{vap}\,A_{drop}(u_{droplet}-u_{vapour})^2$$

The summation is carried out over droplets above the control surface

Additional relations used

$$N(x)=\frac{M}{m_{droplet}\,u_{droplet}(x)}$$

This relates the number density of droplets to M the mass flux density (kg/s/m^2) in the spray

$$\frac{A_{drop}}{m_{droplet}}=\frac{3}{4r_{drop}\,\rho_{drop}}$$

These equations can easily be integrated (numerically) from the origin of the cascade to yield droplet and vapour velocities.

Annex 2: Characteristics of vapour produced by a cascade of winter petrol (Ambient temperature 0°C). Liquid flow rate 550 m^3/hr

The conditions given below are calculated based on equilibrium between the liquid and vapour phases. A given flow rate of liquid is mixed with a given flow rate of fresh air and allowed to reach equilibrium in terms of both temperature and concentration.

Initial liquid composition (Liquid temperature 15°C)

n-butane (as a surrogate for all C4 hydrocarbons) 9.6% wt/wt
n-pentane (as a surrogate for all C5) 17.2% wt/wt
n-hexane (as a surrogate for all C6) 16% wt/wt
n-decane (as a surrogate for all low volatility materials) 57.2% wt/wt

Rate at which air entrained into cascade 96 m^3/s
Final vapour and liquid temperature −8.5°C.

Vapour composition

n-Butane (as a surrogate for all C4 hydrocarbons) 6.0% wt/wt
n-pentane (as a surrogate for all C5) 6.1% wt/wt
n-hexane (as a surrogate for all C6) 2.06% wt/wt
Total hydrocarbons (in air) 14.17% wt/wt

Residual liquid composition

n-butane (as a surrogate for all C4 hydrocarbons) 2.4% wt/wt
n-pentane (as a surrogate for all C5) 11.5% wt/wt
n-hexane (as a surrogate for all C6) 16.3% wt/wt
n-decane (as a surrogate for all low volatility materials) 69.6% wt/wt

Annex 3

	Paraffins						Aromatics				Naphthenes		
Composition % (w/w)	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C6**	**C7**	**C8**	**C9**	**C5**	**C6**	**C7**
Naphtha (worst case)	9	58	20				4				7	2	
Naphtha (typical)	2	56	21	6	1		3	1			2	5	3
Raw gasoline (worst)	2	20	20				35	15	8				
Raw gasoline (typical)	1	9	21				35	13	7	14			
Benzene heartcut			50				50						
Reformate (worst)			22	27	3		21	25	2				
Reformate (typical)			4	18	17	4	5	24	23	5			
Heavy reformate			4	5	3		1	31	34	22			

	Paraffins						Aromatics		Nap
Composition (w/w)	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C6**	**C7**	**C5**
F3 condensate		0.3	4.4	6.5	4.1	6.5	4.7	1.4	2.8
Anusa	0.02	0.4	1.78	2.72	2.3		1.42		0.28
Brent	0.07	0.74	1.75	2.65	2.27	2.84	2.53	1.25	1.5
Arabian		0.57	0.76	1.75	1.53	1.68	1.22	0.37	0.08

The balance of the crude oil mixture is modelled as a range of low volatility alkanes (not shown)

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