

An Extended Procedure to Predict Flammable Cloud Generation Resulting from the Tank Overfilling Scenario

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In 2005, the Buncefield accident showed us that a tank overfilling scenario cannot be treated as a simple liquid spill. After extensive research conducted by HSE, it was established that liquid cascades tended to fragment into droplets and a proportion of the release would form a vapour that could subsequently disperse and if confined, explode. HSE published a Technical Note in 2013 that included a simple mathematical approach to simulate the vapour cloud generation due to evaporation from a cascading liquid. Unfortunately, this empirical approach was limited in its application to a few types of fuels, while the associated explosion prediction also restricted its usage to zero wind conditions and specific congestion situations.

Because the tank-overfilling risks can be relevant to other materials and (weather) conditions as well, Gexcon has expanded the HSE model to calculate the vapour cloud generation due to the overfilling of a tank containing a volatile liquid. The model has been extended to account for the evaporation rate from the generated liquid pool at the bottom, and now incorporates a pure thermodynamic method to calculate the vapour cloud generation of any overflowing flammable liquid.

This way, it has become a pure “source term prediction” method, and now allows the result to be used as input for a subsequent dense gas dispersion phase (which may be subject to certain wind conditions), to evaluate potential explosion risk in any meteorological and confinement situation. Furthermore, the “tank overfilling” model predicts both cloud and pool contents, providing the possibility to calculate the subsequent pool fire event due to direct ignition of the remaining liquid spill.

Typical results of the extended “tank overfilling” method, such as vapour concentrations at the bottom of the liquid cascade, and “cascade” vaporisation rate have been compared with the experimental data and showed very good agreement. The extended “tank overfilling model for cascading liquids” is now available in the Gexcon EFFECTS consequence modelling software. Because the method now also includes the pool evaporation source rate and uses a thermodynamic “droplet evaporation” method, its applicability has been expanded to “non-zero” wind situations, while suitable for any chemical or Hydrocarbon mixture.

1. Introduction

The main objective of the “tank overfilling model for cascading liquids” is to determine if an overfilling operation in a tank can lead to the generation of a flammable cloud. Unfortunately, this potential devastating loss of containment mechanism is often neglected in risk assessments of tank storage operations. Following the investigation of the Buncefield incident in 2005, the publication by (Atkinson and Coldrick, 2012) described the mechanism of this tank overfilling phenomenon. According to this publication, first, the overfilled liquid overtops the deflection plate and falls as a free cascade whilst it also falls close to the wall and may hit a wind-girder (see Figure 1). Second, as the liquid stream accelerates downwards under gravity, it thins, and the surface stress associated with aerodynamic drag increases and the droplets become flattened. This increases the drag, and a catastrophic break-up process into a large number of smaller fragments occurs. This flattening and fragmentation of large droplets is so violent that product droplets are flung outwards in all directions. This produces a rapid expansion in the cascade width and is a main driver of broadening of the cascade throughout its fall. Next, the evaporation of the droplets is driven by the concentration gradient between air and the droplets

surface (Atkinson and Gant, 2018). At the surface of the droplets the vapour pressure is at the saturation condition. Once the vapour pressure in the air has reached this level, no further evaporation can take place. As the liquid falls down in the cascade, it fragments into spray droplets increasing the surface area of the droplets. Vaporization starts to take place in the droplet. The change from liquid phase to vapour phase decreases the temperature of the droplet, thus, forming a cold dense cloud of flammable vapour. The water vapour in the air condenses in the cold vapour cloud due to the low temperature of the cloud, producing a visible mist. Then, at the foot of the tank, the liquid droplets hit the ground forming a splash zone, from which the liquid runs away across the bund floor. The generation of fine splash fragments on impact and the high slip velocities between droplets and vapour lead to greatly enhanced rates of heat and mass transfer in the impact zone. No additional air entrains but the liquid/vapour system is pushed much closer to equilibrium. Finally, since the vapour current is cold and may contain high concentrations of hydrocarbons, the vapour current will be dense and will tend to travel along the ground. If the concentration of the vapour cloud is above its LFL, the cloud may ignite. If the cloud is confined it will also create a vapour cloud explosion (VCE).

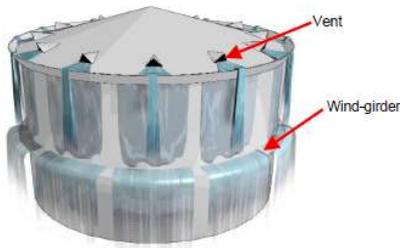


Figure 1: Cascade effect due to tank overfilling

2. Modelling

The implementation of the “tank overfilling model for cascading liquids” in the consequence modelling software EFFECTS has been done based on the mathematical approach described by (Atkinson and Pursell, 2013). This chapter is mainly focused on the description of the expanded and adapted version of this model (see paragraph 2.1 to 2.3).

2.1 Concentration in thermodynamic equilibrium

The model described by (Atkinson and Pursell, 2013) assumes that the vapour concentration of the fuel of study at the gas-liquid interface of the aerosol is in thermodynamic equilibrium with the corresponding liquid component in the droplet. This equilibrium fuel vapour concentration is reached when no further evaporation of the liquid droplets can take place at the foot of the cascade. The model for the calculation of the vaporization from the liquid cascade assumes that they system is adiabatic, that the relative humidity is 100 % and that the wind speed is nil or very low (< 2 m/s) as the experiments in light winds (2-3 m/s) have shown that the vaporisation rate in the cascade is hardly affected by wind speed. (Atkinson and Pursell, 2013) developed a parameterized thermodynamic analysis for a limited amount of chemicals and mixtures. Because this limits the application possibilities to the listed substances, Gexcon decided to expand this with a thermodynamic relation, capable of calculating the concentration of any fuel-composition at the bottom of the cascade. The alternative mathematical approach for the calculation of the fuel vapour concentration proceeds as follows.

Given the mass fraction of the chemical compounds of a mixture, the molar fraction is calculated with Eq(1).

$$x_{i,L} = y_{i,L} \cdot \frac{1}{W_i \cdot \sum(y_{i,L}/W_i)} \quad (1)$$

The heat of vaporisation and saturation vapour pressure of the fuel is calculated with the Antoine equation presented in Eq(2) and Eq(3), respectively. The parameters A, B, C, D and E on the Antoine equation are substance dependent and are available in the EFFECTS' DIPRR chemical database. At this stage of the calculation the droplet temperature it is not known yet. The droplet temperature will be later iterated together with these expressions.

$$L_{v,d} = A \cdot [1 - (T_d/T_c)]^{B+C \cdot (T_d/T_c) + D \cdot (T_d/T_c)^2 + E \cdot (T_d/T_c)^3} \quad (2)$$

$$P_V^{SAT} = \exp(A + B/T_d + C \cdot \ln(T_d) + D \cdot T_d^E) \quad (3)$$

For small droplets, use can be made of Stokes' flow regime which is strictly valid for $Re < 1$ to describe the droplet velocity (see equation 2.145 in (Yellow Book, 1992)), but the results are not sensitive to this assumption (see Eq(4)). The droplet diameter (d_d) is assumed to be 2 mm as this is in good agreement with the droplet diameters seen in the experiments described by (Atkinson and Pursell, 2013).

$$u_d = [(\rho_{l,d} \cdot g)/(18 \cdot \nu_a \cdot \rho_a)] \cdot d_d^2 \quad (4)$$

The liquid heat capacity of air and the thermal conductivity of air are calculated with the Antoine equation described in Eq(5) and Eq(6), respectively.

$$C_{p,a} = A + B \cdot \left(\frac{C/T_a}{\sinh(C/T_a)}\right)^2 + D \cdot \left(\frac{E/T_a}{\cosh(C/T_a)}\right)^2 \quad (5)$$

$$\lambda_a = A \cdot T_a^B / [1 + C/T_a + D/T_a^2] \quad (6)$$

For the calculation of the evaporation from the droplet, first a coefficient k_B is defined which governs the evaporation at the droplets' surface, as described in (Yellow Book, 1992) and shown in Eq(7). Here, $\rho_{L,d}$ is the density of the droplet at the droplet temperature which can be assessed with a form of the Antoine equation shown in Eq(8).

$$k_B = \frac{-4 \cdot W_i \cdot D_c \cdot P_a}{\rho_{L,d} \cdot R \cdot T_a} \cdot \ln\left(1 - \frac{P_V^{SAT}(T_d)}{P_a} \cdot x_{i,L}\right) \quad (7)$$

$$\rho_{L,d} = A / \left[B^{1 + \left(1 - \frac{T_d}{T_c}\right)^D} \right] \quad (8)$$

Next, the temperature difference between the ambient air and the droplet needs to be calculated. This so-called temperature depression as described in Eq(9), maintains the required heat flux from the air to the droplet in order to enable evaporation. The solution needs to be iterative as the saturation vapour pressure (P_V^{SAT}), as included in the evaluation of k_B , the heat of vaporization ($L_{v,d}$) and the liquid density of the droplet ($\rho_{L,d}$) are strongly dependent on the droplet temperature T_d .

$$T_d = T_a - \frac{L_{v,d} \cdot k_B \cdot \rho_{L,d} \cdot \left[1 + 0.28 \cdot Re_d^{\frac{1}{2}} \cdot Sc^{\frac{1}{3}}\right]}{4 \cdot \lambda_a \cdot \left[1 + 0.28 \cdot Re_d^{\frac{1}{2}} \cdot Pr^{\frac{1}{3}}\right]} \quad (9)$$

To calculate the molar vapour fraction in equilibrium at the foot of the cascade (Eq(11)) one shall use Raoult's law as shown in Eq(10). The saturated vapour pressure needs to be calculated at the iterated droplet temperature as described in (Atkinson and Gant, 2012).

$$p_{i,v} = x_{i,v} \cdot P_a = x_{i,L} \cdot P_V^{SAT} \quad (10)$$

$$x_{i,v} = x_{i,L} \cdot (P_V^{SAT}/P_a) \quad (11)$$

Finally, Eq(12) can be used to calculate the mass vapour fraction in equilibrium at the foot of the cascade. As previously mentioned, this mathematical approach allows the assessment of the concentration in thermodynamic equilibrium at the foot of the cascade of any chemical or mixture.

$$C_{fuel} = y_{i,v} = x_{i,v} \cdot \frac{W_i}{\sum(W_i \cdot x_{i,L})} \quad (12)$$

2.2 Inclusion of the pool evaporation phenomenon

The "tank overflowing" model has been expanded to not only include the vaporization rate from the liquid droplets in the cascade but also the vaporization rate from the remaining liquid spill. Therefore it consists of a combined model that contains a "liquid cascade" model and a "pool evaporation" model, and it results in a cumulated vaporization rate which combines the vaporization rate from the cascading liquid with the vaporization rate from the splash products plus the evaporation rate from the liquid pool created at the bottom of the cascade (see

Figure 2). The pool evaporation model is an already existing EFFECTS model which is based on the theory of (Yellow Book, 1992) and the publication by (Trijssenaar-Buhre et al., 2008). Note that the temperature of the pool is assumed to be equal to the droplet temperature as calculated in Eq(10).

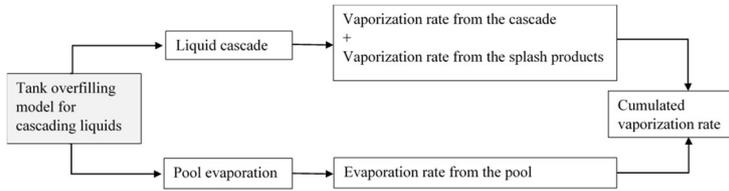


Figure 2: Core calculations of the “tank overfilling model for cascading liquids”

In order to calculate the pool evaporation rate, the amount of remaining liquid M_{spill} , which is creating a pool is determined (see Eq(13)). If there is a bund, the liquid spill generated will be contained within the boundaries of the bund. Otherwise, the liquid spill will spread until the pump feeding the tank is stopped, and hence, the release is terminated.

$$M_{spill} = M_{fuel} - M_{cascade} - M_{splash} \quad (13)$$

M_{fuel} in Eq(14) corresponds to the exiting mass flow rate of the fuel which is overflowing from the tank, $M_{cascade}$ is the vaporization rate of the fuel from the cascade and M_{splash} is the vaporization rate from the splash products generated at the foot of the cascade. The calculation of $M_{cascade}$ and M_{splash} are part of the straightforward mathematical approach described by (Atkinson and Pursell, 2013), which is not the scope of this paper.

The combined vaporization rate is used as the source for the subsequent dense gas dispersion modelling and is calculated as shown in Eq(14), where M_{pool} corresponds to the evaporation rate from the liquid spill. Due to the low temperature this combined source rate $M_{dispersion}$ will always behave as a dense gas.

$$M_{dispersion} = M_{cascade} + M_{splash} + M_{pool} \quad (14)$$

Note that if the chemical or component in the mixture of study has a melting point higher than the droplet temperature, solidification will occur in the liquid spill. In that case, the “tank overfilling for cascading liquids” will skip the pool evaporation calculation as the pool evaporation model is not prepared to handle mixtures containing a solid phase. In that case, only the vaporization from the liquid cascade and from the splash products will be taken into account.

2.3 Adaptation of the model to calculate the dispersion, explosion and pool fire phenomena

The original model as described by (Atkinson and Pursell, 2013) assumes that the vapour cloud would spread along the ground in a concentric manner, where the wind speed would be nil or very low (< 2 m/s). The maximum hazard distance for this gravity forced spreading would be limited only by the volume and height of the cloud. However, Gexcon has adapted the “tank overfilling model for cascading liquids” so that the user can link the model to the EFFECTS “Dense Gas Dispersion Model”. This EFFECTS dispersion model allows the user to account for atmospheric and environment conditions such as wind speed, wind direction, humidity, surface roughness length or Pasquill stability class. This adaptation provides more realistic results for non-zero wind conditions. The user can also link a “congestion area” or an explosion model (e.g., Multi-Energy Model) to the calculated dense gas dispersion model in order to calculate the explosion phenomenon resulting from confinement or congestion of the dispersing vapour cloud. Furthermore, a “pool fire” model can be connected to the “tank overfilling model for cascading liquids” to evaluate the direct ignition of the generated liquid spill.

3. Validation

An alternative thermodynamic method has been developed to calculate the concentration in thermodynamic equilibrium at the foot of the cascade. This method does not need the fitted parameters or the cascade’s reference maximum vapour concentration for the listed chemicals given by HSE’s publication. To validate the calculation method the equilibrium concentration, the results for the vapour concentration at the foot of the tank obtained Gexcon’s approach have been compared with HSE’s approach using the same initial conditions.

First, the two equilibrium concentrations are compared when the temperature of the cloud corresponds to the temperature of storage (as described by the HSE approach). As shown in Figure 3a both Gexcon's and HSE's approach give similar results for the chemical vapour concentration where all the data points are within a 30 % deviation.

Second, the two mathematical approaches are compared while using an altered droplet temperature. The adapted method developed also includes the decrease of the droplet temperature while the chemical starts to vaporize. This phenomenon is not accounted on HSE's approach and due to this higher liquid temperatures, the HSE approach gives significant higher values of the equilibrium concentration compared with the adapted method. (see Figure 3b).

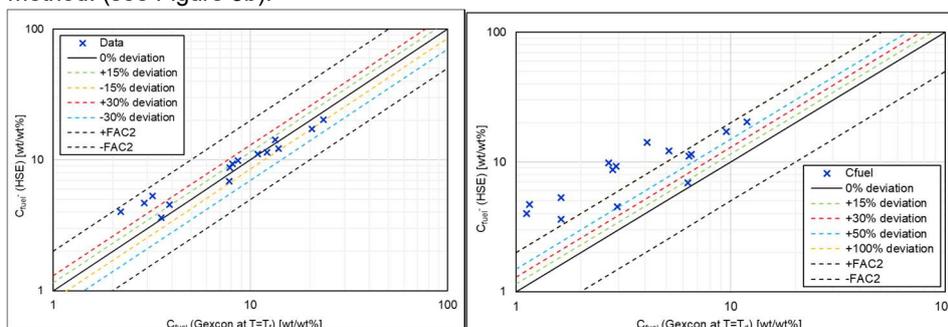


Figure 3: (a) Validation when $T = T_r$ and (b) validation when $T = T_d$

The adapted approach has also been validated against the experimental data described by (Atkinson and Coldrick, 2012) which consisted of 14 large scale cascade experiments (refer to this publication for more information about the experimental conditions). Figure 4a and Figure 4b show the validation of the droplet temperature and the mass vapour fraction in equilibrium at the foot of the cascade, respectively. As shown in Figure 4a, the calculated droplet temperature present deviations of +1 % compared to the experimental data. Figure 4b compares calculated equilibrium vapour mass fraction, illustrating deviations between +10 % and +30 % compared to the experimental data, which is better than the original method which overestimated concentrations to a higher degree.

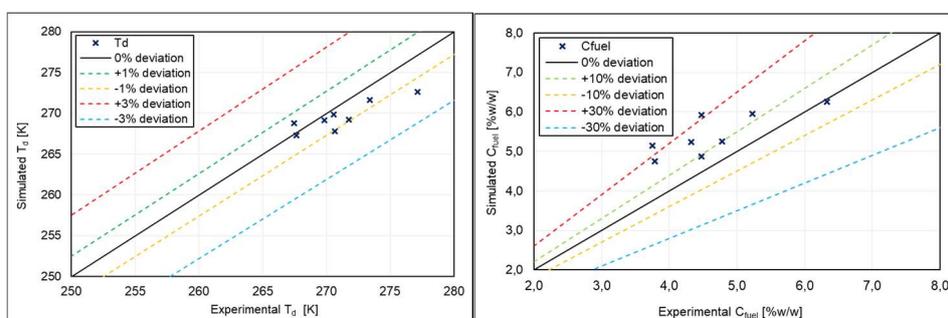


Figure 4: (a) Validation of the droplet temperature and (b) validation of the concentration in thermodynamic eq.

In summary, the mathematical approach described by HSE (Atkinson and Pursell, 2013) estimates the equilibrium vapour concentration at the foot of the cascade at the storage temperature. This concentration is the maximum concentration that can be reached when the mixture is in thermodynamic equilibrium at storage temperature. This constant temperature assumption leads to significant overestimation of the vapour fuel concentration at the bottom of the cascade. This has been improved with the extension of the model with a generalised thermodynamic method that includes the cooling down of the droplets.

4. Conclusions

The “tank overfilling model for cascading liquids” developed by Gexcon and implemented in EFFECTS has been expanded to account for the pool evaporation phenomenon. This provides more realistic results, but might also lead to bigger vapour clouds, specifically when the pool evaporation rate is subject to high wind speeds. The model has also been extended with a thermodynamic method to calculate the vapour cloud generation due to a tank overfilling scenario with any flammable liquid chemical or mixture. This method presents very good

agreement with experimental data. Because the temperature drop of the liquid droplets was not taken into account, the original HSE's approach tends to overestimate the vapour concentration at the bottom of the cascade. The resulting tank overfilling model is a pure source term prediction model, now allowing to include this important loss of containment mechanism to risk assessments of tank storage operations. It predicts both vapour production and liquid pool generation, allowing the calculation of the subsequent dense gas dispersion which may be subject to certain wind conditions, potential vapour cloud explosion, and in case of direct ignition of the remaining liquid spill, the potential pool fire.

Nomenclature

C_{fuel} – fuel concentration, %w/w	Sc – Schmidt number, -
C_{fuel}^* – max. fuel concentration, %w/w	T_a – ambient temperature, K
$C_{p,a}$ – air's heat capacity at T_a , J/(kg·K)	T_b – boiling temperature, K
D_c – vapour binary diffusion coeff through air, m^2/s	T_c – critical temperature, K
d_d – droplet diameter, m	T_d – droplet temperature, K
g – acceleration of gravity (9.8), m/s^2	T_f – storage temperature of fuel, K
k_B – droplet evaporation coeff., m^2/s	u_d – droplet's free fall velocity, m/s
$L_{v,d}$ – heat of vaporisation at T_d , J/kg	W_i – molecular weight of "i", kg/mol
$M_{cascade}$ – vaporisation fuel in cascade, kg/s	x_{air} – mass fraction of air, -
$M_{dispersion}$ – total vaporization rate, kg/s	x_{fuel} – mass fraction of released fuel, -
M_{fuel} – flow rate of fuel, kg/s	x_i – molar fraction (L: liq, V: vap), -
M_{pool} – vaporisation from liquid spill, kg/s	y_i – mass fraction (L: liq, V: vap), -
M_{spill} – flow rate liquid forming pool, kg/s	λ_a – air's thermal conductivity, J/m/s/K
M_{splash} – vaporisation splash products, kg/s	ν_a – air's kinematic viscosity, m^2/s
P_a – atmospheric pressure, Pa	ρ_a – density of air at T_a , kg/m^3
$p_{i,v}$ – partial vapour pressure of "i", Pa	ρ_{cloud} – density of cloud mixed with air, kg/m^3
Pr – Prandtl number, -	ρ_{fuel} – density of cloud at T_d , kg/m^3
P_v^{SAT} – saturation vapour pressure, Pa	$\rho_{L,d}$ – droplet's liquid density at T_b , kg/m^3
R – gas constant 8.31441, J/mol/K	
Re – Reynolds number, -	

References

- Atkinson, G. & Coldrick, S. Vapour Cloud Formation. Experiments and Modelling. HSE report RR908. 2012.
- Atkinson, G. & Gant, S. Buncefield investigation. Liquid flow and vapour production. HSE report RR936. 2012.
- Atkinson, G. & Gant, S. Buncefield Investigation. Dispersion of the vapour cloud. HSE report RR1192. 2018.
- Atkinson, G. & Pursell, M. Vapour cloud development in overfilling incidents. FABIG Technical Note 12. 2013.
- Atkinson, G., Gant, S., Painter, D., Shirvill, L. & Ungut, A. HSE & Shell Global Solutions. Liquid dispersal and vapour production during overfilling incidents. Symposium Series No. 154. 2008.
- Trijsenaar-Buhre, I.J.M, Sterkenburg, R.P., Wijnant-Timmerman, S.I. An advanced model for spreading and evaporation of accidentally released hazardous liquids on land. 2008.
- Yellow Book. Methods for the calculation of physical effects due to release of hazardous materials. CPR14E. 2nd Edition, 1992. The Hague, The Netherlands.