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RISK ASSESSMENT SCREENING STUDY FOR FIRE, EXPLOSION AND TOXICITY EFFECTS OF HYDROCARBONS STORED IN A SPHERE AND BULLET

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Abstract

A fast and economical approach was used to assess impact of fires, explosions and toxicity for a LPG gas storage facility using Fire Explosion and Chemical (FEC) Indices, the TNT and TNO multi energy methods, which are part of a process hazard analysis study. The assessment identified high consequence events for radiation, toxicity and overpressure due to catastrophic rupture of spheres and bullets holding LPG. The FEC Indices indicated that further investigation was needed to determine the extent of blast overpressure whereas toxicity was not identified as a high consequence. The TNO method was used to assess overpressure for congested volumes and unconfined vapour cloud explosions for a bullet, whereas the TNT method was used to predict overpressure occurring on a sphere with no congestion. The FEC indices can be used to screen for high consequence events in order to save time and identify the level of risk complexity needed for process equipment, whereas the TNO method can be easily applied when determining safety distances from LPG facilities for various building constructions provided that the degree of congestion is known.

Keywords: liquefied petroleum gas, fires, boiling liquid expanding vapour cloud explosion, BLEVE, vapour cloud explosion, screening assessment, TNO technique, TNT method

1. Introduction

The LPG market in the world, and especially in Poland, is constantly developing [13]. The liquefied propane-butane mixture is commonly used as fuel for transportation, but also for the other purposes. In 2016 domestic production of LPG in Poland and import of this fuel amounted to 2635 thousands of tons. This scale of use of propane-butane mixtures makes that the safety aspects of storage and the risk assessment associated with possible LPG fires are very important.

The study of boiling liquid expanding vapour cloud explosion (BLEVE) and the inadvertent release and ignition of butane-propane mixtures in congested process facilities, which can cause a vapour cloud explosion (VCE), are of particular interest in the energy sector. A BLEVE is an extremely violent explosion of LPG consisting mainly of a propane-butane mixture. LPG is characterized by an atmospheric boiling point below ambient temperature and therefore stored under pressure in a sphere or a bullet type of vessel. From Lees [11] a BLEVE occurs when a pressure vessel containing a flammable liquid is exposed to fire so that the metal loses strength and ruptures. A BLEVE gives rise to the following effects: (1) blast wave, (2) fragments, and (3)

fireball. A VCE occurs when there is a release of LPG between the upper and lower explosion concentration limits and the mixture is exposed to an ignition source whereas the overpressure strength of the VCE is highly dependent on the degree of confinement from CPQRA [19]. A BLEVE or VCE is one of the most devastating types of explosions, which can result in multiple loss of life and major asset damage. The purpose of a risk screening assessment study is to identify, rank and prioritise critical equipment based on the severity of a BLEVE or VCE, which could lead to overpressure, fire or toxic releases from Gowland [9]. The risk screening study provides the basis of selecting appropriate risk tools when analysing loss of containment scenarios for various hazardous substances, since it is not feasible to investigate all process or storage vessels under pressure with the same depth of analytical rigour when compared to high consequence impacts. Gowland [9] proposes a progressive risk assessment process consisting of four levels of risk estimation beginning from simple and progressing towards more sophisticated risk studies, in order to avoid the rush towards compiling a comprehensive dispersion study and subsequent quantitative risk assessment (QRA).

2. Screening assessment for radiation, toxicity and overpressure

2.1. Assessing fire and toxicity using risk screening tools

Dow Fire and Explosion Index (F&EI) is a Level 1 Risk Review tool from Gowland [9] and widely used to provide a relative value to the risk of individual process unit losses due to fire and explosions, from Mohammad, Mohsen and Mohammad [12]. The (F&EI) is a simple technique to calculate the total risk of the process without requiring highly qualified expertise and its' calculation is not time consuming. The (F&EI) Index analysed by Suardin [15] was used to determine the extent of hazards for the bullets and spheres containing LPG. The (F&EI) index is a dimensionless number that depends on the potential rate of chemical energy release or material factor MF caused by a fire or explosion due to a chemical reaction that is dependent on the flammability and reactivity characteristics – shown in formula (1):

$$F\&EI = MF \cdot F_3. \tag{1}$$

The process unit hazard factor F_3 is a product of factors namely, General Process Hazards F_1 and Special Process Hazards F_2 given in formula (2):

$$F_3 = F_1 \cdot F_2. \tag{2}$$

General Process Hazards F_1 , include exothermic chemical reaction, endothermic processes, material handling and transfer, enclosed or indoor process units, access drainage and spill control whereas Special Process Hazards is a subset of hazards, e.g. combustion flammability limits, relieving pressure, corrosion or toxicity with high probability of an incident that is associated with penalty factors. The Radius of Exposure shown in formula (3) is the radius in [m] in which all equipment in the radius range will be exposed to the potential incident or hazard. For large pieces of equipment, the radius starts from the surface of the equipment while for small equipment the radius starts at the centre of the item considered from [15]:

$$Radius of Exposure = 0.3048 \cdot (F\&EI). \tag{3}$$

The (F&EI) for the sphere and bullet were 246 and 142 respectively indicating heavy to severe fire or explosion, and the hazard exposure radius were calculated as 63 m and 36 m for the sphere and bullet respectively using the Sasol Screening Assessment Tool [20]. Based on the (F&EI) threshold criteria values exceeding 100 the Level 2 Risk Review Study was recommended from Gowland [9] in order to further understand the thermal and overpressure effects of the sphere and bullet.

The Chemical Exposure Index (CEI) is a Level 1 Risk tool with dimensionless quantity and used to measure "relative safeness" of toxic releases from [8]. Computation involves two primary stages namely the first is determining the rate at which the material can become airborne under stipulated process conditions referred to as the airborne quantity release rate, AQ [kg/s]. This parameter depends on the operating temperature and pressure of a process and ambient conditions. The state of the hydrocarbon material just before a release and the diameter of the outlet through which a release is expected, also play significant roles in the specification of airborne quantity and liquid pool area formation. The total airborne quantity release rate AQ is given by the sum of the hydrocarbon airborne quantity evaporation rates derived from the pool surface area and component produced by the flash. When flashing occurs, some liquid will be entrained as droplets. Some of the droplets are quite small and travel with the vapour whereas larger droplets fall to the ground and collect in a pool. As an approximation from Dow [16], the amount of material staying in the vapour is five times the quantity flashed. The second stage involves the calculation of the (CEI) value in formula (4) using the determined value of AQ and the Emergency Response Planning Guidelines (ERPG-2) value published by AIHA from [16]:

$$CEI = 655.1 \cdot \left(\frac{AQ}{ERPG2}\right)^{0.5}.$$
(4)

A simplistic six-step process is used to derive the AQ and (CEI), which is given by Dow [16] for two-phase flow.

Table 1 shows the (CEI) values derived from (4) for propane-butane, and the liquid release rate for pool formation in the event of a sphere or bullet rupture is the main contributor to the (CEI) index, whereas the gas release emanating from the pool formation is insignificant.

Item	Chemical Name	Liquid Release Rate [kg/sec]	(CEI) Index for Liquid Release	Vapour Release Rate [kg/sec]	(CEI) Index for Vapour Release
Spheres	Butane	16.7	27.5	2.62	10.6
	Propane	20.96	48.75	2.28	16.09
Bullets	Butane	11.32	22.61	1.03	6.83

Tab. 1. Chemical Exposure Indices and Release Rates

Since the (CEI) values are less than 100 it indicates low toxicity risk when compared to the trigger criteria for a Level 2 Risk Review study given by Gowland in [9], however exposure to soot inhalation in the event of a fireball can be evaluated through a health risk assessment that is beyond the scope of this article.

2.2. Screening overpressure analysis of the bullet

An approximation VCE screening tool developed by Sasol [21] which is part of the Level 1 Risk Review has found that for typical downstream process plants e.g. refineries, gas or chemicals adopting good engineering practices for facility site layout, and where explosion of a hydrocarbon gas is allowed to pass through in a two dimensional structure, a blast strength curve of six can be used based on the TNO multi energy method from van den Berg [4] for a 500 m³ structure volume when initially evaluating overpressure. The screening VCE tool from [21] was not designed be used to estimate overpressure effects of a BLEVE, which would occur in the sphere containing hydrocarbon gas.

The screening VCE simulation shown in Tab. 2 indicates that the 34.5 kPa overpressure contour occurs approximately 18 m away from the blast for the bullet, which could result in 80%

damage to neighbouring equipment, whereas at 4.6 kPa overpressure located at approximately 116 m from the blast would result in minor damage to un-reinforced buildings in the vicinity of the bullets as described in [21].

Overpressure [kPa]	Radius for Bullet [m]		
4.6	116		
10.3	58		
34.5	18		

Tab. 2. Overpressure Results using Screening TNO Method from [21]

The screening assessments indicate that a Level 2 Risk Review and further analysis are required for the fireball and (BLEVE) overpressure effects for the bullet and sphere based on the (F&EI) and screening overpressure results, whereas the formation of soot can be analysed further using a health risk assessment, which is beyond the scope of this study albeit the (CEI) has low toxicity values for the sphere and bullet.

3. Analytical consequence modelling based on level 2 risk review

3.1. Radiation levels in fireball scenario development

A fireball scenario for a sphere of diameter approximately 14 m containing propane with a butane component of less than 20% is investigated for the thermal and BLEVE effects including probability of fatality. Overpressure of the sphere and radiation is based on equations (5) to (14) with the methodology described by CPQRA in [19]. The maximum and initial Fireball Diameter D_{max} and $D_{initial}$ are derived from (5) and (6):

$$D_{max} = 5.8 \cdot M_{propane-butane}^{1/3} = 403.8 \, m, \tag{5}$$

$$D_{initial} = 1.3 * D_{max} = 524.9 m,$$
 (6)

where $M_{propane-butane}$ is the initial mass of flammable liquid (kg). From [19] the fireball diameter D_{max} and BLEVE duration t_{BLEVE} given in equation (7) do not include the volume of oxygen for combustion, which would vary and affects the size of the fireball. The initial fireball diameter $D_{initial}$ is normally used to describe the initial fireball before buoyancy forces lift it. And it is calculated in equation (6):

$$t_{BLEVE} = 2.59 \cdot M_{propane-butane}^{1/6} = 21.7 \, s.$$
 (7)

Equation (5) is valid for propane-butane mass more than 37000 kg. Height H of fireball can be calculated using formula (8):

$$H = 0.75 \cdot D_{max} = 302.8 \, m. \tag{8}$$

The flux E of approx. 422.2 kW/m² at the surface of the fireball is shown using formula (9):

$$E = \frac{R \cdot M_{propane} \cdot H_c}{\pi \cdot D_{max}^2 \cdot t_{BLEVE}},$$
(9)

where R is given as 0.3, H_c is the heat of combustion for propane-butane, given approx. as 46350 kJ/kg. For a vertically oriented target, the view factor F_{21} is determined using equation (10):

$$F_{21} = \frac{L \cdot \left(\frac{D_{max}}{2}\right)^2}{\left(L^2 + H^2\right)^{3/2}}.$$
(10)

The path length X_s from the surface of the fireball to the target is shown in Fig. 4 and given in formula (11):

$$X_s = (H^2 + L^2)^{0.5} - \frac{D_{max}}{2}.$$
 (11)

The transmissivity τ_a of the atmosphere is given by equation (12):

$$\tau_a = 2.02 \cdot (P_w \cdot X_s)^{-0.09},\tag{12}$$

where P_w is the water vapour pressure given by formula (13):

$$P_w = 1013.25 \cdot RH \cdot exp\left(14.4114 - \frac{5328}{T_a}\right).$$
(13)

RH in the formula (13) is the relative humidity at 80%, and T_a is the ambient temperature at 298 K.



Fig. 4. Geometry for BLEVE Thermal Flux [19]

The received flux at the receptor is calculated from formula (14):

$$I = \tau_a \cdot F_{21} \cdot E. \tag{14}$$

Figure 5 shows the thermal radiation as a function of radial distance starting approx. 200 m away from the centre of the fireball.



Fig. 5. Thermal Radiation versus Horizontal Distance (L) for Sphere Fireball

Note that combustion would be incomplete for radial distances less $D_{max}/2$ since the volume of oxygen present is not included in equations (5) and (7) and a lower heat flux radiation could thus be experienced. The radiation flux for less than 200 m is therefore excluded from Fig. 5.

Damage to process equipment occurs for distances less than 300 m or for radiation flux of more than 37.5 kW/m^{2} , in addition the fire can spread to neighbouring buildings and damage process pipe work for a radius up to 800 m or at a critical radiation intensity greater than 12 kW/m^2 from [11]. According to [5] and [7], the thermal dose TD [(kW/m²)^{4/3}s] probits fatality is given by equations (15) and (16):

$$TD = I^{4/3} \cdot t. \tag{15}$$

Probit for fatality

$$Y_{fatality} = -14.9 + 2.56 \cdot \ln(l^{4/3} \cdot t), \tag{16}$$

It has been found that 50% fatality level is greater than 100 m away and it would only be possible to escape the fireball for distances greater than 1000 m with the risk of blistering from van den Bosch [5], Cozzani, et al [7] and Lees [11].

Radiation arising from the bullet in the event of a rupture is given in the figure below using PHAST Software ver. 6.54 from DNV-GL [17]. The methodology outlined above for the radiation flux can be easily used in small petro-chemical facilities that do not use any commercial process safety consequence analysis software. Fig. 6 shows the fireball effects for the bullet and it can be seen that the heat radiation contours for 37.5 and 12 kW/m² are estimated at approximately 48 and 135 m respectively, resulting in equipment damage and fatality from [11].



Fig. 6. Thermal Radiation versus Horizontal Distance (L) for Bullet Fireball

3.2. Blast overpressure from sphere storing propane-butane mixture

The sphere installation has no blast strength factor since there is no overall blockage and the gas cloud is within parallel plane confinement due to the bund walls with low ignition strength from Behari [3]. The TNT equivalent method described in [19] is used to predict blast overpressure arising from a BLEVE. This requires the chemical energy available in a vapour cloud from the overpressure of the sphere converted to an equivalent mass W of TNT using the formula for isothermal behaviour of ideal gases and ignoring flashing liquid effects shown in formula (17) and given in [19].

$$W = 9.5785 \cdot 10^{-6} \cdot V_{vapour} \cdot {\binom{P_1}{P_o}} \cdot R_g \cdot T_o \cdot \ln {\binom{P_1}{P_2}}, \tag{17}$$

where:

W – equivalent mass of TNT, [kg],

- $P_o -$ the atmospheric pressure, [kPa], $P_o = 101.3$ [kPa],
- P₁ the initial pressure of the compressed gas [kPa], derived as 1.1·1720 [kPa] relief gauge pressure,
- $P_1 = 1993.3$ [kPa absolute],
- P_2 the final pressure of expanded gas, [kPa], $P_2 = P_0 = 101.3$ [kPa],
- T_0 the standard temperature, [K], $T_0 = 298.15$ [K],
- R_g the gas constant, $R_g = 8.314$ [J/(mole·K)],
- V_{vapour} volume of compressed gas [m³], V_{vapour} = 440.06 [m³].

Substituting the values described in the legend gives equivalent TNT mass of W = 612.5 kg TNT. According to [19] the scaled distance Z is given by the following formula (18):

$$Z = {^R/_W}^{1/_3},$$
 (18)

where:

R – the distance from the centre of the blast, [m].

Scaled Overpressure P_s can be calculated according to formula (19) and P_p is the peak pressure, [kPa]:

$$P_s = \frac{P_P}{P_o}.$$
(19)

The relation between scaled overpressure and the scaled distance is shown in [19].

The table shows that fatality due to lung damage will occur within a 20 m radius and neighbouring equipment including building structures would be subjected to minor damage for distances around 300 m for side on overpressures less than 3 kPa from Atkinson, Cusco, Painter and Tam [2].

R [m]	Z [m/kg ^{1/3}]	Scaled Overpressure, P _s	Peak Pressure, P _P [kPa]	Extent of Injury	Fatality Probability %
20	2.34	0.9	91.2	Fatality due to lung damage	95
40	4.71	0.2	20.2	10% Ear drum rupture	25
50	5.88	0.16	16.1	1% Ear drum rupture	25
300	35.32	0.5	2.8	Injuries due to flying glass	10

Tab. 3. Peak BLEVE Overpressure on Sphere using TNT Equivalent Method

The use of the TNT method is based on the following assumptions from T. and S. Abbasi [1]:

1. Flashing fraction of the liquid and the pressurized gas expand isentropically as an ideal gas in a BLEVE;

2. Equates the work done by the expanding vapour with a charge of TNT.

3.3. Blast overpressure from bullet storing propane-butane mixture

The TNO Multi Energy Method developed by van den Berg [4] was used to simulate overpressure contours at various distances from the rupture of the bullet. A 1-dimensional constant flame speed explosion model using numerical integration of compressible flow equations is used to predict blast parameters. The blast parameters use dimensionless energy scaled distance for different initial blast strengths ranging from 1 for insignificant strength to 10 for gaseous detonation. The assumption used in this technique is that a strong blast will occur in a region of the cloud that is subjected to high confinement or congestion whereas the rest of the cloud will burn out without significantly contributing to the blast. The congested or confined portion of the cloud

is modelled separately using a high value ranging from 6 to 10 for the initial blast strength and low values used for the uncongested cloud region that is derived using the TNO blast curves from [4]. The combustion energy assumed is 3.5 MJ/m³ at stoichiometric concentration with air based on a hemispherical hydrocarbon cloud, which is common for most hydrocarbon mixtures. Disadvantages when using the TNO method from van den Bosch [6] are:

- Selection of the Overpressure blast curve in an obstructed region (source strength or class number),
- The definition of an obstructed region,
- The minimal distances between potential explosion' sources for which these sources can be assumed to act independently ('the separation distance').

The disadvantages were addressed considering blast strength factor, ignition strength, and obstacle spacing. A blast strength factor of Low is selected from The Yellow Book [6], defined by an overall blockage less than 30% with spacing between obstacles larger than 3 m for the bullet installation. The gas cloud is within parallel plane confinement due to the bund walls, and the ignition strength is considered high since there is presence of vehicle traffic, within 300 m from the bullet installation. A blast strength index curve of six is thus selected based on the blockage, bund wall geometry and ignition strength for the confined region whereas a blast curve of one is selected for the unconfined area due to the large obstacle spacing more than 3 m, and lower ignition probability away from vehicle traffic.

The equations below describes energy $E_{obstructed}$ and $E_{unobstructed}$ in the congested and uncongested volumes V_{gr} and V_c respectively, scaled distance R, and side on overpressure $P_{S,TNO}$ that were taken from [6]. The values for V_{gr} and V_c were derived from [3] and estimated as 4793 and 50000 m³ respectively.

Energy released in the obstructed area is given from formula (20):

$$E_{obstructed} = E_V \cdot V_{ar} = 16.59 \cdot 10^9 J, \tag{20}$$

where E_V is an energy of combustion of the gas at stoichiometric concentration with air at 3.5 MJ/m³. Similarly, the energy released in the cloud can be calculated with formula (21):

$$E_{unobstructed} = E_V \cdot V_c = 173 \cdot 10^9 J. \tag{21}$$

The scaled blast radius R is given in equation (22):

$$R = r / {\binom{E}{P_0}^{\frac{1}{3}}}, \tag{22}$$

where

r – radius of the location under consideration to the centre of explosion, [m],

E - available energy (Eobstructed or Eunobstructed), [J],

 $P_o - ambient pressure = 101300$ [Pa].

Side on overpressure P_{S,TNO} is calculated in formula (23):

$$P_{s,TNO} = \Delta P \cdot P_o, \tag{23}$$

where

 ΔP – scaled peak side-on blast overpressure from [6].

After calculation of the scaled blast radius R, the side on overpressure are read from blast index curve six applicable for process facility congestion and blast index curve one for the unconfined region that are presented in [6] and discussed in [3]. The Tab. 4 and 5 below show the blast pressure as a function of radius for the obstructed and unconfined vapour cloud explosions. The blast effects in the unobstructed region can cause shrapnel damage, whereas the congested volume indicates side on overpressures that can destroy buildings with 95% fatality levels.

Radius, r [m]	Scaled Blast Radius R	P _{s, TNO} [kPa]	Fatality Probability %	Extent of Injury
50	0.9	50.7	95	Injuries due to flying glass, fatality due to lung damage and 50% ear drum rupture
100	1.8	20.3	25	10% Ear drum rupture
150	2.7	12.2	10	Injuries due to flying glass and 1% Ear drum rupture
400	7.3	3.1	0	Injuries due to flying glass

Tab. 4. Blast Pressure due to BLEVE of Bullet for Obstructed Region Using TNO Method

Tab. 5. Blast Pressure due to BLEVE of Bullet for Unconfined VCE Using TNO Method

Radius, r [m]	Scaled Blast Radius R	P _{s, TNO} [kPa]	Extent of Injury
50	50 0.4		
100	0.8	0.9	Luissian das 45 Chaine altern
150	1.3	0.5	injuries due to flying glass
400	3.4	0.2	

4. Summary of results

The screening assessment results and analytical results are collected and shown in the Tab. 6.

	Screening Assessment Level 1 Risk Review			Analytical Approach Level 2 Risk Review		
	(F&EI) Value	Hazard Effect Radius [m]	Overpressure [kPa]/Radius [m]	Downwind Distance [m] at 37.5 kW/m ²	Overpressure [kPa]/Radius [m]	
Sphere	246	63	Not Applicable	300	91.2 kPa at 20 m	
Bullet	142	36	34.5 kPa at 18 m	50	50.7 kPa at 50 m	

Tab. 6. Screening Assessment and Analytical Results for Radiation and Pressure

The (F&EI) materiality factor provided the highest index of 21 for the bullet and sphere due to the low flash point and boiling point of the mixture followed by the special process hazards factors arising from liquid-gas storage under pressure. The hazard effect radius indicates that all process equipment around 63 m and 36 m away from the sphere and bullet respectively would be exposed to the hydrocarbon overpressure and thermal radiation consequences. The domino effect of neighbouring equipment within the hazard exposure radius would thus need to be included in the Level 1 Risk Review as a separate study. Disadvantages of the TNT method when assessing the sphere rupture is overestimation of the blast overpressure and similar finding was identified by Gexcon, from [18] and earlier by Jiang, Liu and Kim, in [10]. Most BLEVE incidents involving ductile failure, can also be modelled using a revised TNT equivalence method that provides good estimates of blast overpressure based on the fraction of energy released that is converted to a pressure wave described by Planas, Salla and Casal in [14] and Atkinson et al from [2]. The screening overpressure assessment for the bullet provides a less conservative estimate of the blast overpressure based on the assumed congestion of 500 m³ when compared to the analytical approach for values less than 100 kPa since the location specific ignition strength and blockage was not fully approximated when compared to using the analytical approach.

5. Conclusion

The screening assessment provides an easy way to identify high consequence events in the event of a catastrophic release of flammable hydrocarbons under pressure and is able reasonably to assess if domino consequence effects need to be considered based on the hazard effect radius, whereas the FEC indices and screening overpressure results indicated, a Level 2 Risk Review was needed. The TNO technique can be easily used as an effective overpressure analytical tool to determine building safety distances if the location specific ignition strength, obstacle spacing and congestion are well understood, whereas the TNT method was used for modelling overpressure for vessels with no congestion or confinement. The radiation modelling strategy was able to assess complete damage to process equipment in addition to estimating injury or fatality levels without the need of using any commercial software.

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