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Consequence Assessments of a Cold BLEVE. Can We Do It Better?

André Laurent ^{*a,b}, Laurent Perrin ^{a,b}, Olivier Dufaud ^{a, b}

^aUniversité de Lorraine, Laboratoire Réactions et Génie des Procédés, ENSIC, 1 Rue Grandville, BP 20451, F – 54001 NANCY Cedex

^bCNRS, Laboratoire Réactions et Génie des Procédés, UMR 7274, BP 20451, F – 54001 NANCY Cedex andre.laurent@univ-lorraine.fr

Presently in France the control authority (DREAL) in charge of the inspection of the Seveso installations requires the examination of the scenario "cold BLEVE" of very flammable liquid storages (flash point < 273K; vapour pressure > 10^5 Pa at 308K). The proposed case study reports the consequence analysis of a 4,800 m³ spherical isopentane storage tank. The potential cold BLEVE is characterized by a ground level cloud fire associated with a weak fireball tangential to the ground level. Estimations of the explosion energy, blast overpressure and thermal radiation effects were examined with different models. Uncertainties are carefully studied. The prescribed calculation methodology constitutes a basis for administrative decision with important consequences for the safety of population, industry and Land Use Planning.

1. Introduction

Usually, the main hazards associated with the storage and handling of flammable liquids are fire and explosion involving either the liquid and/or the vapour escaping from it. The fire and explosion hazard depends largely on the amount of flammable vapour, which is related to the temperature of the liquid, the amount of the surface area exposed, the duration of exposure and the convection intensity. The hazard also depends on the physical properties of the liquid such as its flashpoint, auto-ignition temperature, upper and lower explosion limits. Among all the explosion phenomena, the BLEVE requires a specific attention due to its major consequences. For example, the literature reports an accident which occurred in a spherical tank of 2,385 m³ containing 1,843 m³ of mixed pentane and hexane at a Texas refinery. Over an hour after the original fire was initiated, the top of the tank ruptured violently and the storage BLEVEd: 19 fire-fighters were killed and 31 injured (IFW, 2006). The severity greatly depends on the liquid temperature and specifically whether it is greater than the superheat limit temperature (SLT) or not (Hemmatian et al., 2014). In the previous instance, the SLT value was reached, but "cold BLEVE" can also occur for temperature lower than the SLT. Sometimes neglected with respect to "hot BLEVE", the examination of a "cold BLEVE" scenario is now required for very flammable liquid storages by the control authority (DREAL) in charge of the inspection of the Seveso installations in France.

2. Description of the case study

In order to assess the consequences of a cold BLEVE and analyse the uncertainties of some predictive models, a case study based on a 4,800 m³ spherical tank filled at 85 % with iso-pentane has been developed. Isopentane (CAS number 78-78-4) has numerous industrial applications such as fuel, fuel additive, solvent, aerosol propellant in cosmetics formulation, blowing agent for polystyrene or in a catalyst mixture used in the manufacture of high density polyethylene... But isopentane is an extremely volatile and flammable hydrocarbon. Its main properties are listed in Table 1. The tank, stored at room temperature (293 K) and 2.5 bar, is heated by an engulfing fire. The results of some classical models assessing the overpressure and radiation effects will be compared with regard to the reference values of threshold for effects on people, imposed by the French major risk regulation (Table 2). The thermal impact of a BLEVE is function of its duration and the radiation received.

Table 1: Isopentane properties

| Physical properties | | Thermochemical properties | |
|-----------------------|---|-----------------------------|---|
| Liquid density: | ρ _L = 625 kg.m ⁻³ | Liquid spec. heat capacity: | C _{PL} = 2.77 x 10 ³ J.kg ⁻¹ . K ⁻¹ |
| Vapour density: | $\rho_V = 2.931 \text{ kg.m}^{-3}$ | Vapour spec. heat capacity: | C_{PV} = 3.39 x10 ⁵ J.kg ⁻¹ .K ⁻¹ |
| Critical temperature: | T _C = 460 K | Heat capacity ratio: | γ=1.074 |
| Critical pressure: | P _C = 33.3 bar | Combustion heat: | $\Delta H_{\rm C} = 4.524 \text{ x } 10^7 \text{ J.kg}^{-1}$ |
| Boiling temperature: | T _{EB} = 300 K (at 1.013 bar) | Vaporization heat: | $\Delta H_V = 3.390 \times 10^5 \text{ J.kg}^{-1}$ |
| Flammability limits: | LFL = 1.4 % | | |
| | UFL = 7.6 % | | |
| Flashpoint: | FP = 222 K | | |
| Auto-ignition temp.: | AIT = 693 K | | |

Table 2: Overpressure and thermal radiation threshold values adopted in France

| Human effects | Irreversible | 1% lethal | 5% lethal |
|--|--------------|-----------|-----------|
| Overpressure (mbar) | 50 | 140 | 200 |
| Thermal effects (kW/m ²) ^{4/3} .s | 600 | 1000 | 1800 |

3. The classical BLEVE theory

Consider a spherical storage, equipped with two pressure relief valves, containing isopentane at 293 K and 2.5 bar(a) (point A in Figure 1). Due to the thermal radiation from a fire, the temperature increases to T_R i.e. 330 K (point B). Under these conditions, if the vessel bursts (due to the failure of the material or an impact, for example), there will be an instantaneous depressurization from 2.5 bar to the atmospheric pressure P_0 . At this pressure, the temperature of the liquid-vapor mixture will be 330 K (point D) and the depressurization process will correspond to the vertical line BD. As this line does not reach the SLT line tangent to the saturation curve at the critical point (393 K at 1 bar), the conventional theory states that there will be no BLEVE, strictly speaking (Laboureur et al., 2014). Nevertheless, there will be a strong instantaneous vaporization and even an explosion, but nucleation in the liquid core will not occur: this phenomenon is called a cold BLEVE. It should be noted that the limiting temperature of superheated liquid obtained here for isopentane by using the tangent line method (393 K) is rather consistent with the calculations and experiments of Shebeko and Shebeko (2015), i.e. 416 and 412 K respectively.

This conventional theory, although accepted by many authors, fails to explain some of the BLEVEs that have occurred. In fact, the SLT tangent method is only based on thermodynamical considerations, and its use to predict a BLEVE occurrence involves taking into account a safety margin. Eckhoff (2014) notably stressed that the SLT line is not an absolute lower temperature limit for a BLEVE to occur. However, it is clear that the blast overpressure generated by such BLEVEs will be considerably lower than those produced by BLEVEs occurring above the SLT also called hot BLEVEs.



Figure 1- Pressure – temperature curve and Superheat Limit Temperature line for isopentane.

4. Predicting the effects of cold BLEVEs

There are mainly three types of BLEVE effects: the overpressure wave, the thermal radiation and fragments projection (Abbassi and Abbassi, 2007). In risk analysis, often, only the thermal radiation from the fireball is considered. However, the blast overpressure can be very strong especially at short distances, notably for low

fill levels, and should not be neglected. This paper focuses on both overpressure and thermal effects as the main events of a cold BLEVE scenario.

4.1 BLEVE overpressure modelling

The BLEVE overpressure is usually modelled using generalized methods based on thermodynamic equations. All these methods consist first in the calculation of the expansion energy based on the change in thermodynamic state of the fuel, i.e. from its initial storage state to the final state at boiling temperature and atmospheric pressure. This expansion energy is then used in the calculation of a scaled distance (\bar{R}) based on the TNT equivalent mass, also expressed as Sachs scaled combustion charge. Overpressure can be then determined by graphical or numerical methods (CCPS, 1994; TNO, 1997). Nevertheless, the estimation of the overpressure is subjected to various uncertainties, the main ones being associated to the amount of energy released, the fraction of this energy devoted to the blast, the relative contribution of pre-existing vapour and flash vaporization (Hemmatian et al, 2014). Indeed, it is very difficult to estimate the contribution of the respective phases of the boiling liquid and the expanding vapour. Furthermore, a portion of the energy is used up in shattering the storage, another one in propelling the fragments and only the remaining energy is transmitted to the blast wave. Finally, the simultaneous cooling effect of the flash vaporization of the liquid and the expansion of the storage of the scenario.

The theoretical flash fraction F of isopentane is thus given on the basis of isenthalpic analysis by equation (1):

$$F = 1 - \exp[C_{PL} (T_{EB} - T_R) / \Delta H_V]$$

This fraction of released liquid which has been vaporized (here F=0.21) is a poor prediction of the total mass of fuel in the vapour cloud, because of the possible presence of spray and aerosol formation (CCPS, 1994). A common practice for estimating aerosol formation is to assume that the aerosol fraction is equal to a multiple β of the flash fraction, typically 1 to 3. In the case of a cold BLEVE, the initial temperature being lower than the SLT, this fraction will be lower than for a hot BLEVE scenario.

Hasegawa and Sato (1977) have reported for pentane that, when the theoretical percentage of flash evaporation exceeds 36%, the released liquid burns virtually as a fireball. This indicates that, as a rough guide, the mass of liquid entrained is about twice the mass of the vapour produced by the flash. On the other hand, when the percentage was in the range of 20 to 36% (as it is the case here), a part of the fuel was consumed for the fireball and the remaining part burnt on the ground like a pool fire. At last, most fuel burnt on the ground when the percentage was in less than 20%. According to CCPS (1994) and assuming a linear or exponential variation of the correcting factor versus the flash fraction, the value β applied in this case study will be 2.6.

4.1.1 Models based on TNT equivalent mass.

The equivalent charge weight of TNT is then calculated using the following equation:

$$E_{TNT} = \propto \frac{m \, \Delta H_C}{W_{TNT}} \tag{2}$$

where α is the yield or efficiency factor and W_{TNT} the blast TNT energy (4.68 MJ/kg). For external explosions, a yield factor of 0.01 to 0.03 (recommended by HSE) can be applied. The side-on peak overpressure of the blast wave at some distance R can be found from the conventional TNT equivalency model with the scaled distance:

 $\bar{R} = R / E_{TNT}^{0.33}$

Results of the TNT modelling concerning our case study are presented in Table 3 with the distance to specific overpressure for the respective flash situation (α =0.03 and F=0.21), flash and aerosol combined case (α =0.01 and 0.03 with F=0.21) and worst case (α =0.03 and F=1).

| Table 3: TNT | model prediction | n of the distance | es R (m) to th | he specified | overpressures. |
|--------------|------------------|-------------------|----------------|--------------|----------------|
| | | | \ / | , | |

| Overpressure (mbar) | \bar{R}_{TNT} | R flash α=0.03 | R flash-aerosol α=0.01 | R flash-aerosol α=0.03 | R worst case α=0.03 |
|------------------------|-----------------|-------------------|---------------------------|---------------------------|------------------------|
| 50 | 24.3 | 1332 | 1270 | 1832 | 3388 |
| 140 | 9.4 | 505 | 481 | 694 | 1284 |
| 200 | 7.3 | 392 | 374 | 539 | 997 |

The use of the classical and simple TNT method implies some limitations. Indeed, this model is based on the hypothesis that a potential explosion of a gas cloud is proportional to the total amount of fuel present in the cloud, whether it is within its flammable limits or not. Predicting a plausible yield for the explosion is also

(3)

difficult. The TM 5 – 1300 diagram is based on experiments with condensed explosives, but the blast wave produced by a gas explosion does not exhibit the same shape. Despite these drawbacks, the attractiveness of the TNT model lies in the direct empirical relation between the charge weight of TNT and resulting damage. But the model remains a poor model for the gas explosion blast and should not be used in situations in which major incident conditions occurs and for Land-Use Planning purposes.

Laboureur et al. (2013) have so compared the predictions from the different models with data corresponding to the experiments at laboratory scale, small scale, midscale and large scale. The predictions from Prugh (1991) model, which considers an isentropic expansion of the cloud, and from Casal and Salla (2006) model gave the best estimations of the overpressure. However, Prugh predictions are better suited for a conservative approach. Table 4 shows an example of the predictions obtained with these two models. In the simple method of Casal and Salla, the fraction of the available energy devoted to a quick estimation of the overpressure is calculated between two limits corresponding by the respective isentropic and irreversible thermodynamic process (i.e. the yield factor ranges from 5 to 15 %).

| Overpressure (mbar) | R _{PRUGH} (m) | R _{CASAL} (m) isentropic | R _{CASAL} (m) irreversible |
|---------------------|------------------------|-----------------------------------|-------------------------------------|
| 50 | 503 | 431 | 306 |
| 140 | 191 | 264 | 116 |
| 200 | 148 | 127 | 90 |

4.1.2 Models based on fuel – air charge blast

The TNO Multi-Energy Model (MEM) presents a set of curves which relate the dimensionless overpressure $\overline{P} = P/P_0$ to the combustion energy scaled distance calculated as follows: $\overline{R} = \frac{R}{(E/P_0)^{0.33}}$, where E is the charge combustion energy. Alonzo et al. (2006) have fitted the characteristic curves \overline{P} versus \overline{R} by use of power equations. A safe and conservative estimate of the blast strength can obviously be made if a maximum strength of 10 is assumed. However, a strength of 7 seems to be more accurate to represent actual experiments carried out in congested zones. If the cloud is unconfined and uncongested an initial strength *i* of 2 (quiescent) or 3 to 5 is recommended (CCPS, 1994). Some results are tabulated for the overpressure threshold values described in Table 2 (Table 5).

| Overpressure | (mbar) R flash | R flash + aerosol | R flash + aerosol | R worst case |
|--------------|----------------|-------------------|-------------------|--------------|
| | i = 3 | i = 3 | i = 5 | i = 3 |
| 50 | 309 | 511 | 2011 | 625 |
| 140 | (-) | (-) | 711 | (-) |
| 200 | (-) | (-) | 511 | (-) |

Table 5: TNO MEM model prediction of the distances R (m) to the specified overpressures

The reported methods gave considerably different results when applied to the isopentane storage. The TNT method systematically predicts notably stronger blast effects than the MEM method. As already mentioned, the estimation of the overpressure is subjected to numerous uncertainties, especially related to the determination of the flash fraction, which could be significantly lower for a cold BLEVE than for a hot BLEVE scenario.

4.2 BLEVE thermal radiation

According to Abbasi and Abbasi (2007), the following parameters must notably be determined to enable the prediction of the size (H and R_B), duration t_B and thermal radiation of a fireball q_R : i) the mass of flammable substance released during the BLEVE, ii) the mass of flammable substance consumed in the fireball, iii) the fireball development as a function of time, iv) the view factor.

Numerous models have been published to estimate these parameters. They can be grouped in three different approaches: static models (CCPS, 1994; TNO, 1997), dynamics models (Martinsen and Marx, 1999) and the Shield model (1993).

Static models do not take into account the temporal evolution of the fireball. The two most widely used are the models developed by the CCPS and the TNO. The radiation from the fireball received by an observer at a given distance from the source is usually modelled through a solid flame model. The TNO model for radiation is expressed in equations (4-9), where SEP is the Surface Emissive Power:

| $q_R = SEP F_G \tau$ | (4); | $F_G = R_B^2 / (X^2 + H^2)$ | (5); | $H = R_B = 3.24 \ m^{0.325}$ | (6); |
|---|------|-----------------------------|------|------------------------------|------|
| $SEP = \frac{m f_S \left(\Delta H_C - \Delta H_V\right)}{4\pi R_B^2 t_B}$ | (7); | $f_S = 0.00325 P_V^{0.32}$ | (8); | $t_B = 0.852 \ m^{0.26}$ | (9) |

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In the same way, the set of equations of the CCPS model is expressed in equations (4, 5, 10-13):

$$H = R_B = 2.9 \ m^{0.333} \quad (10); \qquad SEP = \frac{m f_S \ \Delta H_C}{4\pi R_B^2 \ t_B} \quad (11); \qquad f_S = 0.27 \ P_{RUP}^{0.32} \quad (12); \qquad t_B = 2.6 \ m^{0.167} \quad (13)$$

The dynamic models have similar formulations as the static models, but take into account the temporal evolution. For example, Martinsen and Marx (1999) developed the following set of equations (4, 5, 12, 14-16):

$$H = R_B = 2.9 \ m^{0.333} \ (14); \qquad SEP = \frac{m f_S \ \Delta H_C}{0.3888 x 4 \pi R_B^2 \ t_B} \ (15); \qquad t_B = 0.9 \ m^{0.25} \ (16)$$

This dynamic model considers the fireball as a sphere which diameter increases with time and remains tangent to ground as it grows. At the end of the growth phase, at $t_B/3$, the fireball has reached its maximum diameter (D=2.R_B). The emissive power SEP is estimated with a time averaged surface area of the fireball. Shield model (1993) is quite complex and the details are included in the cited publication. Figure 2 illustrates a schematic comparison of the time evolution of the fireball dimensions and SEP between three modelling approaches.



Figure 2 – Fireball models: schematic evolution of diameter (continuous line), height H (dotted line) and SEP (dash line) with time. Left: static model – Middle: dynamic model – Right: Shield model (Laboureur, 2012)

Laboureur (2012) reported that the TNO model is simpler to use compared to the dynamic models or the Shield model and it gives good estimates for the fireball diameter and duration. For the radiation, the same author recommended the modelling approach of Martinsen and Marx (1999).

The three previous models were applied to the calculation of the thermal radiation from an isopentane cold BLEVE with a liquid flash (F=0.21), an aerosol correction of β =2.6 and a transmissivity τ equals to 0.75. Table 6 summarizes the radius of the fireball, its duration, the fraction of the generated heat radiated from the flame surface and the Surface Emissive Power of the flame surface.

| Model | CCPS | TNO | Martinsen and M |
|---------------------------|------|------|-----------------|
| Radius R _B (m) | 322 | 322 | 322 |
| Duration $t_B(s)$ | 28 | 34 | 31 |
| f (-) | 0.17 | 0.17 | 0.17 |
| SEP (kW/m ²) | 293 | 219 | 181 |

Table 6: Characteristics of the fireball flame

There is a great variability in the estimated SEP values obtained with the three models, which is not the case for the other parameters. The value of SEP calculated with the dynamic model is a mean value taking into account the evolution of the fireball with time. Another possibility is to use an arbitrary SEP value of the literature in the range of 200 to 350 kW.m⁻², but it obviously implies huge uncertainties. It should be noted that Hasegawa and Sato (1977) reported for a fireball of n-pentane a SEP value of 100 kW.m⁻² at a pressure of 2.5 bar.

Table 7: Respective static models CCPS –TNO and dynamic model predictions of the distances d (m) to the specified thermal radiations values

| Thermal effects | d _{CCPS} | d _{TNO} | d Martinsen and Marx |
|--|-------------------|------------------|----------------------|
| 600 (kW/m ²) ^{4/3} .s | 1478 | 1369 | 1193 |
| 1000 (kW/m²) ^{4/3} .s | 1206 | 1116 | 967 |
| 1800 (kW/m²) ^{4/3} .s | 948 | 874 | 752 |

arx

Table 7 reports the ground distances d (m) on a vertical human receptor from the flame BLEVE at the French thermal radiation threshold values with the three models.

5. Conclusions

Based on the analysis presented is this paper, the following general conclusions can be drawn about the uncertainties with regard to the estimated consequences of a potential cold BLEVE of isopentane. First, by comparing the modelling results, it appears that the estimated distances differ by 30% for overpressure effects (without considering the classical TNT model) and 20% for the thermal radiation effects. These uncertainties lies in particular in the fact that the empirical equations used in the investigated classical models resulted from multiscale experiments carried out mainly with LPG, which limits the representativeness for the other chemical substances such as isopentane. Moreover, the first evaluation step of the amount of combustible contributing to the fireball is crucial. It has notably been demonstrated that the flash fraction is a key parameter to assess the consequences such explosive phenomenon. However, this parameter depends essentially on the difference between the initial temperature TR (caused by the engulfing fire) and the boiling temperature of the fuel. It seems then necessary to take the difference between TR and the SLT into account to quantify the amount of liquid vaporised and to distinguish the effects of a cold BLEVE from those of a hot BLEVE.

To sum up, it appears important to reduce the uncertainties in the estimation of the size of the fireball, of the duration of the phenomenon, of the charge combustion energy and of the SEP of the flame to improve the modelling of the overpressure and thermal radiation of a BLEVE. Nevertheless, recent publications focusing on the comparison of the different models with varied experimental data are deficient, especially when cold BLEVE scenarios have to be considered. This remains an area where a great deal of further R&D is required. The different consequence assessment methods should be described with argued commentaries on their relative merits and accurate conditions of their application.

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