

Using liquid superheating energy for a quick estimation of overpressure in BLEVEs and similar explosions

Joaquim Casal^{a,*}, Josep M. Salla^b

^a Department of Chemical Engineering, Centre d'Estudis del Risc Tecnològic (CERTEC), Universitat Politècnica de Catalunya, Diagonal 647, 08028-Barcelona, Catalonia, Spain

^b Department of Heat Engines, Universitat Politècnica de Catalunya, Diagonal 647, 08028-Barcelona, Catalonia, Spain

Received 5 April 2006; received in revised form 28 April 2006; accepted 2 May 2006

Available online 9 May 2006

Abstract

A method is proposed for the quick estimation of the peak overpressure caused by a Boiling Liquid Expanding Vapor Explosion (BLEVE) or a similar explosion. The method is based on the use of the “superheating energy” (SE), which is the difference between the specific enthalpy of the liquid at the temperature just before the explosion and the specific enthalpy of the liquid at its saturation temperature, at atmospheric pressure. The analysis performed with a set of reference substances showed that in a BLEVE or in similar explosions, the energy converted into overpressure will range between 3.5 and 14% of SE. The comparison of the values thus obtained with experimental data from the literature shows a fairly good agreement.

© 2006 Elsevier B.V. All rights reserved.

Keywords: BLEVE; Explosion; Superheat limit temperature; Superheating energy; Overpressure

1. Introduction

Among the various types of pressurized tank explosions that can occur, Boiling Liquid Expanding Vapor Explosions (BLEVEs) are one of the most severe. Even though BLEVEs frequently involve flammable substances (hydrocarbons), and are thus followed by a fireball of even worse consequences, the mechanical explosion may also cause severe damage due to the pressure wave and the ejection of missiles.

For this reason, a significant effort has been made to study BLEVE explosions over the last decade. Several researchers have published articles concerning the diverse aspects of these accidents, such as the mechanisms of explosions [1], the influence of thermal stratification [2], and the behavior of ejected fragments [3]. Our knowledge about the phenomenon has significantly improved, although not sufficiently. There are still wide gaps in our knowledge, such as the real influence of superheating on the mechanism and dynamics of the explosion, and the assessment of the resulting overpressure.

Almost the same thing happens in explosions whose less intense degree of superheating might be interpreted as not constituting a BLEVE—although this will ultimately depend on the accepted definition of a BLEVE.

The severity of the explosion – and, therefore, its consequences – varies according to the mass of material involved, the conditions (pressure/temperature), and the properties of the substance. Diverse methods have been proposed to estimate the overpressure caused by explosions, all of which are somewhat complex. Substantial benefits would obviously be derived from devising a simple method for the rapid evaluation of the effects of a BLEVE.

This is the objective of this paper. A new approach was adopted for tackling the superheat limit temperature, which is based purely on energy considerations, resulting in a parameter that makes it possible to assess the overpressure of a potential BLEVE or a similar explosion.

2. Explosion and superheat limit temperature

Fig. 1 is a schematic representation of a vessel containing a liquid in equilibrium with its vapor at temperature T and the corresponding vapor pressure P (significantly higher than atmo-

* Corresponding author. Tel.: +34 934016704; fax: +34 934017150.
E-mail address: joaquim.casal@upc.edu (J. Casal).

Nomenclature

d	distance from the centre of the vessel to the point at which the overpressure must be calculated (m)
d_n	normalized or scaled distance ($\text{m kg}^{-1/3}$)
h_g	enthalpy of vapor at temperature T (kJ kg^{-1})
h_{g0}	enthalpy of vapor at T_0 (kJ kg^{-1})
h_l	enthalpy of liquid at $T_{\text{sl-E}}$ or at the temperature in the vessel just before the explosion (kJ kg^{-1})
h_{l0}	enthalpy of the liquid at T_0 (kJ kg^{-1})
m_l	mass of liquid (kg)
P	pressure (kPa)
P_0	atmospheric pressure (kPa)
$P_{T_{\text{sl-E}}}$	saturation pressure at $T_{\text{sl-E}}$ (kPa)
ΔP	peak overpressure (kPa)
q_l	heat released by the liquid (kJ kg^{-1})
q_v	vaporization energy (kJ kg^{-1})
SE	“superheating energy” of liquid (kJ kg^{-1} or MJ m^{-3})
T	temperature (K)
T_0	boiling temperature of liquid at atmospheric pressure (K)
T_s	boiling temperature of liquid at pressure P (K)
T_{sl}	superheat limit temperature (K)
$T_{\text{sl-E}}$	superheat limit temperature from energy balance (K)
U	internal energy (kJ kg^{-1})
ΔU	variation of the internal energy of vapor (kJ kg^{-1})
V	volume of vapour (m^3)
ΔV	volume variation of vapor (m^3)
W_i	isentropic work associated to vapor expansion (kJ kg^{-1})
W_0	irreversible expansion work of vapor (kJ kg^{-1})
W_{TNT}	equivalent mass of TNT (kg)
x	vaporization fraction of the initial mass of liquid

Greek letters

β	fraction of the energy released converted into a pressure wave
ρ_l	liquid density at the temperature just before the explosion (kg m^{-3})

spheric pressure). If the vessel is depressurized instantaneously to atmospheric pressure P_0 , the liquid will reach a state in which it will be at temperature T , at a pressure P_0 , which is much lower than its corresponding equilibrium pressure P , and the liquid can be described as being superheated and in a metastable state. One moment later, the situation will have developed to the – immediate – final condition (Fig. 1c) in which thermodynamic equilibrium is attained. That is, a fraction of the liquid will have vaporized, taking the required energy from the remaining liquid, which will not have undergone any change of state but will have cooled.

Depending on the initial conditions just before the explosion, it is possible that the liquid be at the so-called superheat

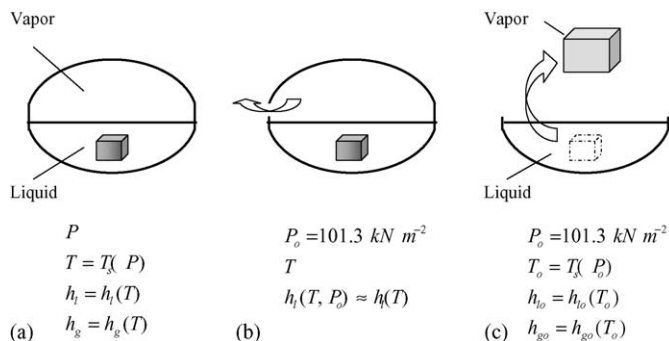


Fig. 1. Liquid–vapor equilibrium under sudden depressurisation at constant temperature.

limit temperature (T_{sl}). According to certain authors [4], T_{sl} is the minimum temperature that, due to the degree of superheating, would guarantee a homogeneous nucleation process in the whole liquid mass. According to this theory, this would be the required condition for a BLEVE explosion. The value of T_{sl} was traditionally obtained using thermodynamic equilibrium methods by applying an equation of state (such as the Redlich-Kwong equation).

A recent work [5] has shown that T_{sl} can be obtained by adopting quite a different approach, involving an energy balance performed on the liquid contained inside the vessel that bursts. The temperature thus obtained, $T_{\text{sl-E}}$ which corresponds to the situation in which the energy transferred from the cooling liquid to the vaporizing liquid has its maximum value – which implies a minimum energy content in the remaining liquid – is equivalent to T_{sl} . $T_{\text{sl-E}}$ corresponds to a vaporization fraction $x = 0.5$, and can be easily obtained from an energy balance applied to a unit mass of liquid. In an adiabatic vaporization process, the fraction of liquid that is vaporized can only obtain the required energy from the remaining liquid mass that is cooled. If q_v is the required vaporization energy per unit mass (kJ kg^{-1}), it can be expressed as a function of the enthalpy according to the following expression:

$$|q_v| = h_{g0} - h_l \quad (1)$$

where h_{g0} is the enthalpy of saturated vapor at T_0 and h_l is the enthalpy of liquid at T .

If q_l is the heat (also per unit mass, kJ kg^{-1}) that can be released by the remaining liquid fraction when it is cooled from the initial temperature to the boiling temperature at atmospheric pressure (T_0), it can be expressed as:

$$|q_l| = h_l - h_{l0} \quad (2)$$

where h_l and h_{l0} are the enthalpies of the liquid at temperatures T and T_0 , respectively.

q_l will increase with the difference $T - T_0$ (the superheating degree of the liquid), while q_v will decrease as $T - T_0$ increases. Therefore, there will be a temperature $T_{\text{sl-E}}$ at which the following expression will be true:

$$|q_v| = |q_l| \quad (3)$$

i.e.:

$$h_{g0} - h_1 = h_1 - h_{10} \quad (4)$$

This expression allows us to calculate the superheat limit temperature T_{sl-E} at which the vaporizing liquid fraction is equal to the fraction of liquid that does not undergo any change of state and is cooled.

3. Energy released in the explosion and “superheating energy”

The severity of the explosion depends on the ensuing overpressure. Peak overpressure is usually estimated as a function of the energy released, and this is calculated as the adiabatic work resulting from the expansion of the vaporizing liquid. This work is calculated as the difference between the values of the initial and final energy values of the process; therefore, even if the initial state is the same, the work found will differ according to the path followed—for example, whether or not the process is assumed to be a reversible adiabatic process.

Nevertheless, in all cases the superheating energy (SE) contained in the superheated liquid with respect to its final state immediately after the explosion (i.e. in equilibrium with its vapor at atmospheric pressure) will be the energy that will be partly converted to work to build the overpressure. Therefore, it seems quite logical to consider this superheating energy as an indicator of the severity of a given explosion.

In this analysis, for simplicity we did not take into account the contribution of the expansion of the vapor already existing inside the vessel just before the explosion, which is considered to be negligible compared to the contribution of the liquid vaporization.

Taking into account that the variation of enthalpy between two liquid states is very similar to the variation of energy, the difference of enthalpy values on the right-hand side of Eq. (4) can be assumed to be the superheating energy of a liquid superheated at a temperature T (or, under very specific conditions, at T_{sl-E}) compared to the energy that it would have if it was in equilibrium

at the temperature T_0 , i.e.

$$SE = h_1 - h_{10} \quad (5)$$

For a selected group of substances, and for their respective values of T_{sl-E} , Table 1 shows the corresponding saturation pressure, liquid density at T_{sl-E} , and the “superheating energy” of the liquid per unit mass and per unit volume, respectively.

To study the relationship between the superheating energy of the superheated liquid and the adiabatic work in the explosion, we also calculated the work associated with reversible adiabatic expansion (the isentropic work, $W_i = \Delta U$; U is the internal energy) of the vapor generated and the expansion work against the atmospheric pressure (an irreversible process, $W_o = P_o \Delta V$; P_o is the atmospheric pressure and V is the volume). The procedure described by Planas et al. [6] was applied. In the first case, the energy of the final state was calculated for a state defined by the atmospheric pressure and entropy equal to that of the initial state. In the second case, the final state was defined by the atmospheric pressure and the relationship $W_o = P_o \Delta V$. The values thus obtained are included in Table 1.

The superheating energy per unit volume corresponding to the diverse substances (for the specific case of $T = T_{sl-E}$) is plotted in Fig. 2 in order to highlight the differences between one substance and another. It can be observed that 1 m^3 of water heated up to its T_{sl-E} has a superheating energy, that is seven times that of 1 m^3 of propane at its corresponding T_{sl-E} . Ammonia, methanol and ethanol also have relatively high SE values, while the remaining substances – mostly hydrocarbons – have lower values.

The saturation pressure associated with a given temperature can also be considered to be an indicator of the severity of the explosion, which is in fact equivalent to T . In Fig. 3, the pressure (again for the specific case of $T = T_{sl-E}$) corresponding to each substance is plotted. Again, a significant variation can be seen from one substance to another.

The equivalence of T_{sl-E} and $P_{T_{sl-E}}$ as explosion severity indicators can also be observed in Fig. 4, in which $(P_{T_{sl-E}} - P_o)$ is plotted as a function of $(T_{sl-E} - T_0)$ for a set of substances. Each substance is differently located to the others. From a practical

Table 1
Superheating energy per unit mass and per unit volume, for different liquids at a temperature T_{sl-E}

	T_{sl-E} (K)	$P_{T_{sl-E}}$ (kPa)	$\rho_{l,T_{sl-E}}$ (kg m^{-3})	$SE_{m,T_{sl-E}}$ (kJ kg^{-1})	$SE_{V,T_{sl-E}}$ (MJ m^{-3})	W_i (kJ kg^{-1})	W_o (kJ kg^{-1})
Water	606.4	13357.0	632.5	1131.0	715.4	319.9	83.0
Nitrogen	118.6	2389.0	533.3	97.0	51.7	28.4	10.6
Ammonia	375.2	6507.0	450.9	684.1	308.4	187.0	55.7
Methane	174.7	2696.0	297.8	258.3	76.9	72.3	26.4
Ethane	271.2	2273.0	404.9	248.6	100.6	62.9	23.6
Ethylene	257.2	2799.0	402.4	241.7	97.3	65.4	23.4
Propane	315.3	1434.0	463.6	212.2	98.4	49.4	20.6
Propylene	314.7	1689.0	474.6	221.4	105.1	52.0	21.1
<i>n</i> -Butane	348.8	927.7	506.1	191.5	96.9	39.6	18.5
<i>n</i> -Pentane	378.8	659.7	525.5	180.4	94.8	32.3	16.7
<i>n</i> -Hexane	407.6	541.4	541.1	163.4	88.4	28.6	15.6
<i>n</i> -Heptane	429.9	425.1	554.3	160.9	89.2	24.3	14.2
<i>n</i> -Octane	453.0	359.0	559.3	156.3	87.4	21.2	13.6
Methanol	483.0	4768.0	520.3	540.6	281.3	131.6	40.7
Ethanol	465.0	2518.0	572.1	419.6	240.0	84.1	29.8

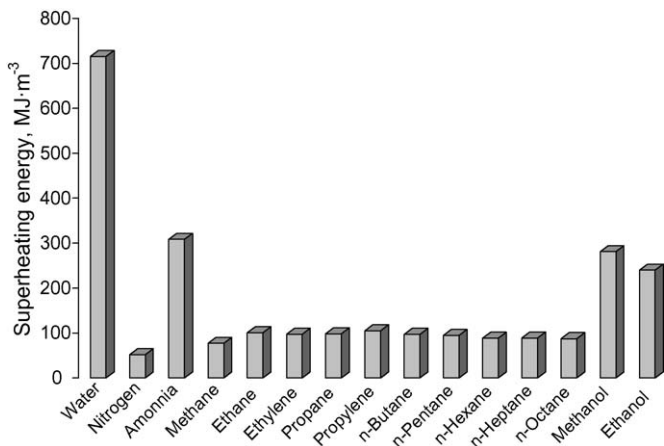


Fig. 2. Superheating energy for several substances (it has been calculated assuming the liquid temperature was T_{sl-E}).

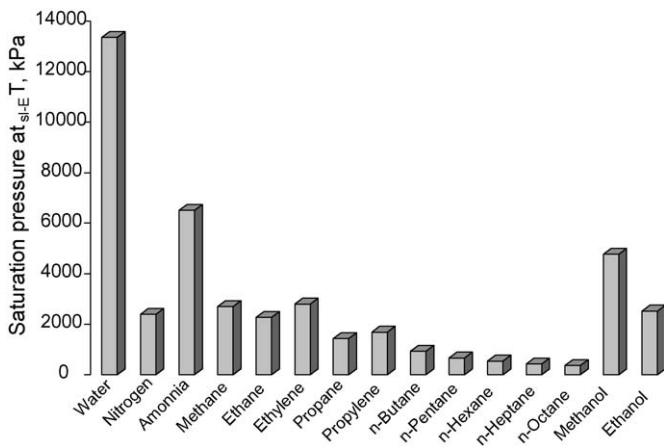


Fig. 3. Saturation pressure associated to T_{sl-E} for different substances.

point of view, we can assume that the closer a substance is to the origin of the coordinates, the more likely it will be to reach its uppermost limit (superheating limit), but less energy will be released when an explosion takes place. This is the case, for example, of hydrogen, *n*-octane or *n*-heptane. Instead, water is

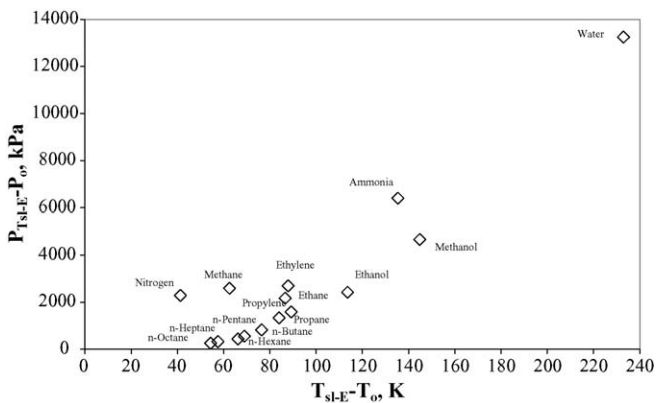


Fig. 4. The diverse substances in a $P_{T_{sl-E}} - P_0$ vs. $T_{sl-E} - T_0$ plot. As the distance of origin of coordinates increases the released energy converted into overpressure increases.

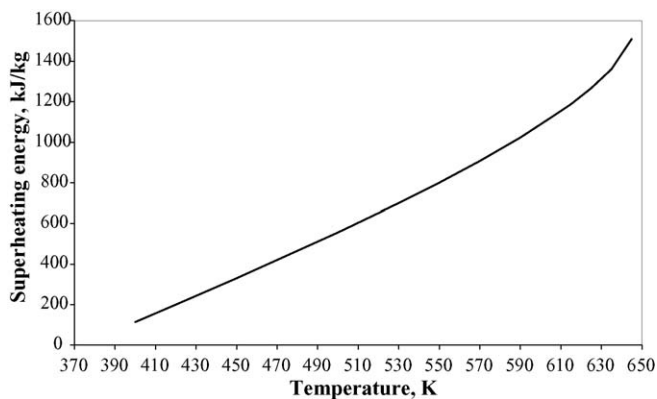


Fig. 5. Variation of superheating energy as a function of temperature for water. It can be seen that high values of SE are reached even at temperatures below the superheat limit temperature.

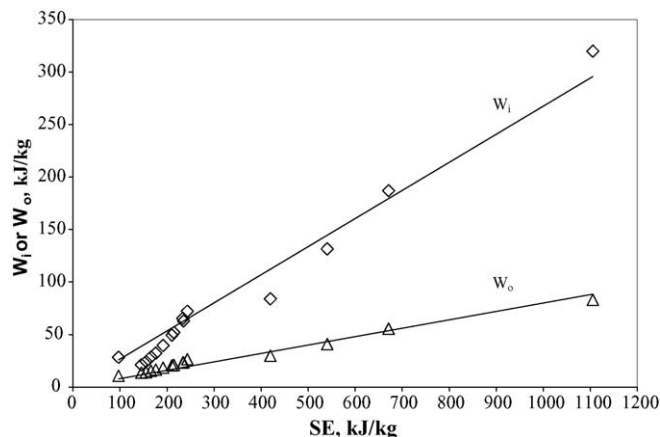


Fig. 6. Isentropic work and expansion work against atmospheric pressure as a function of the liquid superheating energy for diverse substances (Table 1).

in the opposite situation: a major increase in temperature (and pressure) is required to reach the superheating limit, but the final explosion will release a very large amount of energy even at temperatures below T_{sl-E} .

Superheating energy increases, of course, with liquid temperature. In Fig. 5, SE is plotted as a function of T for water, showing the high energy content at temperatures even below T_{sl-E} (606.4 K).

Finally, the isentropic expansion work and the expansion work against the atmospheric pressure were plotted as a function of the superheating energy of the liquid (Fig. 6). A clear correlation exists in both sets of data, indicating again that SE could be used as an indicator of the severity of potential explosions.

Although Figs. 2–4 and 6 correspond to liquids at their respective superheat limit temperature T_{sl-E} , similar conditions can be expected of a superheated liquid (i.e. at a temperature higher than its boiling temperature at atmospheric pressure) at any temperature.

4. Overpressure as a function of SE

The ratio between the energy converted in the pressure wave and SE was calculated for both the isentropic and the irre-

Table 2

Percentage of superheating energy converted into overpressure for both isentropic and irreversible processes (the values have been calculated for the specific case in which the liquid was at T_{sl-E})

Substance	$SE_{m,T_{sl-E}}$ (kJ kg ⁻¹)	W_i (kJ kg ⁻¹)	$SE_{m,T_{sl-E}}$ (%) in ΔP (isentropic)	W_o (kJ kg ⁻¹)	$SE_{m,T_{sl-E}}$ (%) in ΔP (irreversible)
Water	1131	319.9	14	83	3.7
Ammonia	684.1	187	13.7	55.7	4.1
Methane	258.3	72.3	14	26.4	5.1
Ethane	248.6	62.9	12.7	23.6	4.7
Ethylene	241.7	65.4	13.5	23.4	4.8
Propane	212.2	49.4	11.6	20.6	4.9
Propylene	221.4	52	11.7	21.1	4.8
n-Butane	191.5	39.6	10.3	18.5	4.8
n-Pentane	180.4	32.3	9	16.7	4.6
n-Hexane	163.4	28.6	8.6	15.6	4.8
n-Heptane	160.9	24.3	7.6	14.2	4.4
n-Octane	156.3	21.2	6.8	13.6	4.4
Methanol	540.6	131.6	12.2	40.7	3.8
Ethanol	419.6	84.1	10	29.8	3.6

versible process. To do this, the “useful” energy of the explosion (columns 6 and 7 in Table 1) was multiplied by 0.5 (it is usually accepted that in the ductile breaking of a vessel, approximately 50% of the released energy is converted into overpressure [7]), divided by the SE and finally multiplied by 100 to express it as a percentage. These percentages can be seen in columns 3 (isentropic process) and 5 (irreversible process) in Table 2.

To take into account the ground effect (in a practical case, the explosion will take place at the surface of the earth or slightly above it), these percentages should be multiplied by two to account for reflection of overpressure wave on ground. However, if this effect has already corrected in the TNT curve used to determine ΔP [8], this correction is not required.

By analyzing these data, it can be observed that for an isentropic process, the energy devoted to overpressure ranges between 7 and 14% of SE, while for an irreversible process it ranges between 3.6 and 5%.

To compare SE with the peak overpressure once more, the ΔP was calculated for the different substances in Table 1 assuming that there was a temperature of T_{sl-E} just before the explosion. The calculation was performed for two different masses and a given distance. The method of TNT equivalent mass was applied [6], with the following value for the scaled distance:

$$d_n = \frac{d}{(\beta W_{TNT})^{1/3}} \tag{6}$$

where $\beta=0.5$ and W_{TNT} is the equivalent mass of TNT. The peak overpressure was obtained from the plot of ΔP versus d_n [8]. The ΔP was calculated for the following situations: liquid mass = 100 kg, $d = 50$ m, and liquid mass = 10,000 kg and $d = 50$ m (Fig. 7). As can be observed, there is a clear correlation (logarithmic) between the ΔP and SE. A calculation example has been included in Fig. 8.

We have not introduced any factor to correct the effect of the tank shape, as we consider that this effect is not well

known and is very difficult to quantify. However, any reader could introduce a tank-shape correction by his own on the final result.

To further test the estimations made by using SE, they were compared with the scarce experimental data found in the literature. Birk [9] obtained peak overpressures in the range of 2–10 kPa for the explosion of a propane tank of 0.4 m³; from the SE value, overpressures of 6–16 kPa are found. Giesbrecht et al. [10] measured peak overpressures of 300–400 kPa at a distance of 10 m for the explosion of a tank containing 452 kg of propylene; by using the SE method, we obtained 200–300 kPa. Moreover, Stawczyk [11] used masses of 11 kg of propane–butane to obtain much higher ΔP values than those obtained by the method proposed in this paper. We believe that this discrepancy can be attributed to the fact that in his experimental work, the temperature just before the explosion was much higher than T_{sl-E} and, therefore, SE was also much higher.

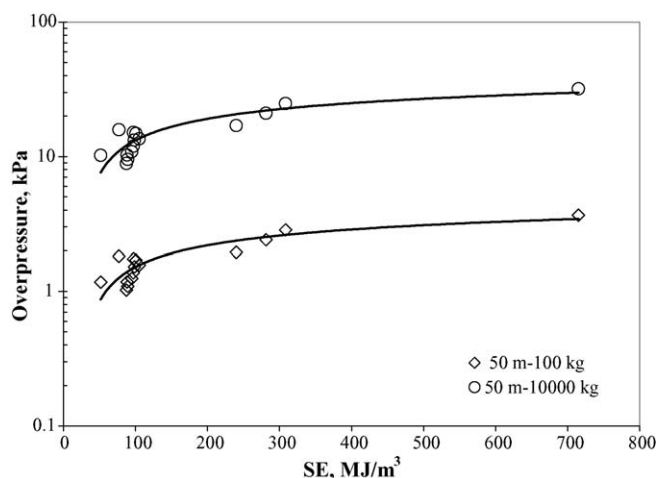


Fig. 7. Variation of peak overpressure as a function of SE for two different cases.

Example of calculation of ΔP

Suppose the explosion of a vessel containing 2,000 kg of liquid water at $T = 553$ K and $P = 64.24$ bar ($h_l = 1236.5$ kJ kg⁻¹). Estimate ΔP at a distance of 50 m.

Additional data: $h_{l0} = 418.9$ kJ kg⁻¹; amount of TNT required to release 1 MJ = 0.214 kg.

$$SE = 1236.5 - 418.9 = 817.6 \text{ kJ kg}^{-1}$$

$$2000 \text{ kg} \cdot 817.6 \text{ kJ kg}^{-1} = 1635205 \text{ kJ}$$

a). If an isentropic process is assumed, the maximum energy converted into overpressure will be the 14% of SE :

$$1635205 \text{ kJ} \cdot 0.14 = 228930 \text{ kJ}$$

and the equivalent mass of TNT:

$$M_{TNT} = 228930 \cdot (0.214 \cdot 10^{-3}) = 49 \text{ kg}$$

The scaled distance will be:

$$d_n = \frac{50}{\sqrt[3]{49}} = 13.7 \text{ m kg}^{-1/3}$$

Which gives an approximate peak overpressure (using ΔP vs. d_n plot of Van den Berg and Lannoy (1993)) of 0.1 bar.

b). If an irreversible process is assumed, the maximum energy converted into overpressure will be the 5% of SE , and then the following values are obtained:

$$\text{Maximum energy converted into overpressure} = 1635205 \text{ kJ} \cdot 0.05 = 81760 \text{ kJ}$$

$$M_{TNT} = 81760 \cdot (0.214 \cdot 10^{-3}) = 17.5 \text{ kg}$$

$$d_n = 19.2 \text{ m kg}^{-1/3}$$

$$\Delta P = 0.068 \text{ bar}$$

Fig. 8. Example of calculation of ΔP .

5. Conclusions

The severity of an explosion associated with the sudden depressurization of a superheated liquid is a function of the “superheating energy”, i.e. the difference between the specific enthalpy of the liquid at the temperature just before the explosion and the specific enthalpy of the liquid at its saturation temperature at atmospheric pressure. SE is essentially the energy released in the explosion. In the case of the ductile breaking of the vessel, approximately 50% of SE is available to cause the pressure wave.

The fraction of this available energy that will be devoted to create the overpressure will depend on the thermodynamic ensuing process. If it is assumed that the process is isentropic – impossible in practice, but accepted by some authors who take a conservative position – this fraction will be higher than if an irreversible process is assumed. In fact, these two processes – isentropic and irreversible – establish the higher and lower limits of the range of values for the energy converted into overpressure.

The analysis performed with a set of reference substances showed that in a BLEVE or in similar explosions, the energy converted into overpressure will range between 7 and 14% of SE if an isentropic process is assumed. If an irreversible

process – less conservative but more realistic – is assumed, this range is approximately 3.5–5%. This allows a quick estimation of the ΔP for a given vessel to be made, if its content and its temperature, just before the explosion are known.

The comparison of the values thus obtained with experimental data from the literature shows a fairly good agreement.

References

- [1] J.E.S. Venart, Boiling liquid expanding vapor explosions (BLEVE); possible failure mechanisms and their consequences, in: IChemE Hazards XV, Symp. Ser. No. 147, 2000, pp. 121–138.
- [2] Y.W. Gong, W.S. Lin, X.S. Gu, A simplified model to predict the thermal response of PLG and its influence on BLEVE, J. Hazard. Mater. A108 (2004) 21–26.
- [3] M.R. Baum, Failure of a horizontal pressure vessel containing a high temperature liquid: the velocity of end-cap and rocket missiles, J. Loss Prevent. Process Ind. 12 (1999) 137–145.
- [4] R.C. Reid, Possible mechanism for pressurized-liquid tank explosions or BLEVE's, Science 203 (1979) 1263–1265.
- [5] J.M. Salla, M. Demichela, J. Casal, BLEVE: a new approach to the superheat limit temperature, J. Loss Prevent. Process Ind., in press.
- [6] E. Planas-Cuchi, J.M. Salla, J. Casal, Calculating overpressure from BLEVE explosions, J. Loss Prevent. Process Ind. 17 (2004) 431–437.

- [7] D.A. Crowl, J.F. Louvar, *Chemical process safety – Fundamentals with Applications*, Prentice Hall PTR, New Jersey, 2002.
- [8] A.C. Van den Berg, A.C. Lannoy, Methods for vapor cloud explosion blast modeling, *J. Hazard. Mater.* 34 (1993) 151–171.
- [9] A.M. Birk, Hazards from propane BLEVE's: an update and proposal for emergency responders, *J. Loss Prevent. Process Ind.* 9 (1996) 173–181.
- [10] H. Giesbrecht, K. Hess, W. Leuckel, B. Maurer, Analysis of explosion hazards on spontaneous release of inflammable gases in the atmosphere. Part 1: propagation and deflagration of vapor clouds on the basis of bursting tests on model vessels, *Ger. Chem. Eng.* 4 (1981) 305–314.
- [11] J. Stawczyk, Experimental evaluation of LPG tank explosion hazards, *J. Hazard. Mater.* B96 (2003) 189–200.