EVALUATION OF THE UN VENT SIZING METHOD FOR ORGANIC PEROXIDE PORTABLE TANKS

J A Hare* and W D Adams**
*   Health and Safety Laboratory, Buxton, Derbyshire, SK17 9JN
**   Hazardous Installations Division, Health and Safety Executive, Merseyside L20 3RA

Type F organic peroxides are permitted for transport in portable tanks. Emergency Relief Systems have to be fitted to tanks intended for the transport of such peroxides. The United Nations Manual of Tests and Criteria includes a method to determine the minimum required emergency vent area using a 10 dm^3 test apparatus. The 10 dm^3 test apparatus is electrically heated (to simulate a fire) and the vent area is then scaled-up on vessel volume.

The Design Institute for Emergency Relief Systems (DIERS) has also produced methods to size the vents for gas generating runaway reaction systems including the decomposition of organic peroxides. These methods make use adiabatic calorimeters and vent sizing equations that consider if the vent will have to pass a two-phase gas-liquid flow or a single-phase gas-only flow.

The UN vent sizing method is evaluated and large-scale trials on organic peroxide decomposition described. DIERS vent-sizing calculations for two-phase homogeneous flow and gas-only flow are compared with the large scale test results.

Keywords: organic peroxides portable tanks, emergency relief systems, vent sizing.

INTRODUCTION

Runaway chemical reactions, if not adequately prevented or mitigated, can give rise to major accidents (e.g. Seveso, Bhopal). Pressure relief (venting) is a commonly used method of mitigation which, if properly designed, will prevent failure of the vessel, thereby averting a major accident.

Type F organic peroxides, which may undergo self accelerating decomposition, can be transported in tanks or intermediate bulk containers (IBCs) provided that these are fitted with adequately sized emergency pressure relief devices. The current state of the art for the design of pressure relief systems for runaway chemical reactions has been developed following research by the Design Institute for Emergency Relief Systems (DIERS) research consortium in the USA (Fisher et al[1]). However, the United Nations Manual of Tests and Criteria (UN[2]) includes a test method "Example of a Test Method for Vent Sizing", to determine the "required emergency vent capacity to be fitted to a specific portable tank for a particular organic peroxide". This method involves determining the critical orifice diameter by electrical heating (at a rate to simulate fire engulfment) of the peroxide in a 10 dm^3 vessel and then using area to volume scaling to calculate the minimum vent area for the tank. Experts in vent sizing have expressed serious doubts as to the applicability of this method.

However, as the method is relatively easy to apply, it is being increasingly used. The Hazardous Installations Division of HSE therefore commissioned HSL to perform an evaluation of the UN method in order to establish whether and under what circumstances it may be unsafe.

DANGEROUS GOODS TRANSPORT

UK legislation on the transport of dangerous goods implements two European Council directives (94/55/EC and 96/49/EC) which require EU member states to align their domestic transport legislation within the provisions of ADR (ECE[3]) and RID (ECE[4]). ADR is the European agreement concerning the international carriage of dangerous goods by road and RID is the European agreement concerning the international transport of dangerous goods by rail. As there is so much international trade in goods, there are agreements which control the way in which such goods are transported internationally. The UN Recommendations on the Transport of Dangerous Goods (UN[5]) forms the basis for the main European agreements for the transport of dangerous goods by road (ADR) and rail (RID) and international agreements for the transport of dangerous goods by sea (IMO) and air (ICAO).

UN VENT SIZING METHOD

The UN vent sizing method is based on some experimental work which indicates that, for organic peroxide formulations, the ratio of the minimum emergency vent area to the tank capacity is constant and can be determined using a reduced scale tank of 10 dm^3 capacity. DIERS methodology suggests that area to volume scaling applies only if the phase and density of the material vented is the same at both scales. A small-scale test may vent a gas-only flow, whereas a large-scale test may vent a two-phase flow. The higher density of the two-phase release requires the vent to carry a larger mass flow and so the vent must be considerably larger than application of the simple area to volume scaling would suggest.

The UN Model Regulation 4.2.1.13 permits the transport of type F organic peroxides in portable tanks. Model Regulation 4.2.4 has a table listing all organic peroxide mixtures which are permitted for transport in portable tanks. The possibility of self-accelerating decomposition and fire engulfment should be taken into account for tank transport of organic peroxides (Model Regulation 4.2.1.13.2). Tanks intended for the transport of organic peroxides should be fitted with emergency relief devices (Model Regulation 4.2.1.13.6). The emergency relief device (Model Regulation 4.2.1.13.8) should be designed to vent all decomposition products and vapours evolved during a period of not less than one hour of complete fire engulfment as calculated by the formula:

$$q = 70961 \, F \, A^{0.82} \tag{1}$$

and where F = 1 for non insulated vessels and, for insulated vessels, is given by:

$$F = U \, (923 - T_{PO}) \, / \, 47032 \tag{2}$$

The set pressure of the emergency relief device is set above that of the pressure relief device used for non-emergency situations. The emergency device is dimensioned so that the maximum pressure in the tank never exceeds the test pressure of the tank (Model Regulation 4.2.1.13.8). The minimum test pressure for a portable tank should be 4.0 barg (Model Regulation 4.2.1.13.4). The pressure relief device (normally a bursting disc) is designed to prevent any pressure build up in the portable tank due to decomposition products and vapours at a temperature of 50°C (Model Regulation 4.2.1.13.7). Bursting disc pressures are normally set in the range 3.0 to 3.5 barg so that they do not activate unnecessarily during transport. The UN method (Manual of Tests and Criteria - Appendix 5) is given as an example method of how to determine the size of the emergency relief device. Other methods may be used provided that they adequately size the emergency relief device. The 10 dm^3 UN tests would be undertaken to provide data for the design of emergency relief devices for the particular

tank concerned. For insulated portable tanks the capacity of the emergency relief device shall be determined assuming a loss of insulation from 1% of the surface area (Model Regulation 4.2.1.13.9).

Complete fire engulfment was defined in the 1994 test method as a heat load of 110 kW m^{-2}; so that the heat absorption was proportional to the wetted area. The current definition for compete fire engulfment is based on API 520 (API[6]) without prompt fire fighting or good drainage; here the heat load is proportional to the wetted area to the power of 0.82. The heating rate to be used in the UN test is calculated from the sum of the heat load directly and indirectly to the exposed surface.

The UN test apparatus consists of a stainless steel tank with a gross volume of 10 dm^3 which is fitted with an extra bursting disc (set at 80% of the design pressure of the 10 dm^3 vessel) for safety reasons. The 10 dm^3 tank is fitted with a 1 mm opening which simulates the tank PRV (this is scaled using vent area to tank volume ratio) and a bursting disc assembly with a variable aperture orifice plate which simulates tank emergency venting (also scaled using vent area to tank volume ratio). The outer surface of the tank below liquid level is heated at a constant rate independent of the heat generated by the peroxide. A method is given to calculate the heating rate to be used in the test. The temperatures in the liquid and gas phase are measured as well as the tank pressure. The UN test vessel is unlikely to fail catastrophically during the testing process because of the protection of the extra bursting disc and also the largest diameter orifice available is used in the initial testing.

The minimum or suitable portable tank vent area (A_p) is calculated from the minimum orifice vent area (A_t) determined in a test in which the maximum pressure is not more than the test pressure of the portable tank, where the test vessel has volume (V_t) and the portable tank (V_p):

$$A_p = V_p \, (A_t \, / \, V_t) \tag{3}$$

DIERS VENT SIZING METHODOLOGY

For gassy systems the vent is designed for the maximum rate of gas evolution which generally occurs at the maximum temperature (Leung[7]). This is because there is no latent heat for cooling and thus the reaction temperature is not controlled by venting. A volumetric balance is achieved with the maximum volumetric gas generation rate being equal to the volumetric discharge rate. The relationship can be represented as:

$$(dQ/dt)_{g,max} = W \, / \, \rho_e \tag{4}$$

The volumetric gas generation rate is evaluated based on the experimental measurement of the rate of pressure rise data in a small scale adiabatic calorimeter. The maximum rate of gas evolution is obtained from the experiment using:

$$(dQ/dt)_{g,max} = (m_o \, / \, m_t \,) \, (V_f \, / \, P_m) \, (dP/dt)_{max} \tag{5}$$

There are now two approaches to calculate the mass flow rate (W) that the vent should be able to deal with: firstly and more rigorously to assume a two-phase relief and secondly to assume a gas only relief.

HOMOGENEOUS TWO-PHASE RELIEF

The exiting fluid density can be calculated from the vessel average density, which assumes homogeneous vessel venting, thus:

$$\rho_e = m_o / V \tag{6}$$

The required mass flowrate, W, is then calculated as:

$$W = \rho_e \, (dQ/dt)_{g,max} = (dQ/dt)_{g,max} \, (m_o / V) \tag{7}$$

Thus the ideal vent area (A), which is calculated from the required mass flowrate and the vent capacity (G), is:

$$A = (W / G) = (dQ/dt)_{g,max} \, (m_o / V \, G) \tag{8}$$

The mass flux G can be calculated using the Omega solution for the Homogeneous Equilibrium Model (HEM) (Leung[8]). A gassy system will generate a non flashing flow (since no vapour is being generated) with the value of omega lying between 0 and 1. The basic Omega equation is:

$$G = G^* \, (P_o \, \rho_e)^{1/2} \tag{9}$$

GAS-ONLY RELIEF
Here the exiting fluid density is calculated as for an ideal gas:

$$\rho_e = \rho_g = P \, M_W / R \, T \tag{10}$$

The gas mass flux can be calculated using equation 9:

$$G = G^* \, P \, (M_W / RT)^{1/2} \tag{11}$$

G^* equals 0.61 for an isentropic coefficient (k) value of 1.0 for choked isothermal flow, which is the worst case. Choked flow is the maximum flow rate of a compressible fluid (gas or two-phase) for a given upstream pressure.

We can now calculate the vent area using equations (4) and (11):

$$A = W/G = (dQ/dt)_{g,max} \, \rho_e / \, G^* \, P \, (M_W / RT)^{1/2} \tag{12}$$

Then using equation (10) to replace the exiting fluid density:

$$A = (dQ/dt)_{g,max} \, (M_W / RT)^{1/2} / G^* \tag{13}$$

Thus for choked flow:

$$A = ((dQ/dt)_{g,max} / 0.61) \, (M_W / RT)^{1/2} \tag{14}$$

FAUSKE'S RECENT GASSY EQUATION
Fauske[9,10] argues that the vent area may be calculated as for an ideal gas (13). Fauske then assumes that the critical value of G^* equals 2/3 instead of the true value of 0.61 and also introduces a discharge coefficient (C_D) to obtain:

$$A = (3/2) \, ((dQ/dt)_{g,max}/C_D) \, (M_W/RT)^{1/2} \tag{15}$$

Then substituting equation (5) into equation (15):

$$A = (3 / 2\ C_D)\ (m_o\ V_f\ (dP/dt)_{max} / m_t\ P_m)\ (M_W/RT)^{1/2} \tag{16}$$

The initial mass in the reactor can be calculated in terms of the reactor volume and the reactant density (Note equation (17) assumes that the vessel is always liquid full):

$$m_o = V\ \rho_r \tag{17}$$

Thus an expression for the vent area per unit volume can be obtained:

$$A/V = (3 / 2\ C_D)\ (\rho_r\ V_f\ (dP/dt)_{max} / m_t\ P_m)\ (M_W/RT)^{1/2} \tag{18}$$

HARE'S SIMPLIFIED GASSY EQUATION
This simplified vent sizing equation uses the DIERS[1] gassy equation and takes account of two phase flow. The equation solves the DIERS gassy vent sizing equation (equation 8) with the mass flux G calculated using a reliable two-phase flow method. The maximum rate of gas evolution can be calculated from the small scale maximum pressure rate using the temperature corrected version[1] of equation (5), which is reproduced here:

$$(dQ/dt)_{g,max} = (m_o/m_t)\ (V_f/P_m)\ (dP/dt)_{max}\ (T_t/T_c) \tag{19}$$

A suitable equation is required to calculate the two-phase (gas / non-flashing liquid) flow characteristic of gassy systems (Etchells and Wilday[11]). One approach is to use the Omega method (Leung[8]):

$$G = G^*\ (P_o / v_e)^{1/2} \tag{20}$$

Using the Omega method for a gassy system requires knowledge of the vessel void fraction (α_o) and the isentropic coefficient of the gas (k) as omega would be calculated as:

$$\omega = \alpha_o / k \tag{21}$$

Graphs of G^* and critical pressure ratio (η_c) versus Omega are available and the Omega method also allows corrections to be made for friction and backpressure. An alternative approach is to use Tangren's method (Tangren *et al.*[12]), which although it assumes isothermal flow instead of the adiabatic flow assumed by the Omega method, gives very similar results for choked flow. For this simplified analysis, choked flow will be assumed. Tangren's method requires the critical pressure ratio (Leung & Fauske[13]) to be calculated first:

$$\eta_c = \left[2.016 + \left(\tfrac{1-\alpha_0}{2\alpha_0}\right)^{0.7}\right]^{-0.714} \tag{22}$$

where α_o is the void fraction entering the relief system from the upstream vessel. The value of G, using Tangren's method, can now be calculated:

$$G = \sqrt{\tfrac{P_0}{v_e}}\ \frac{\left(\tfrac{2}{\alpha_0}\left[\left(\tfrac{1-\alpha_0}{\alpha_0}\right)(1-\eta)-\ln\eta\right]\right)^{0.5}}{\tfrac{1}{\eta}+\left(\tfrac{1-\alpha_0}{\alpha_0}\right)} \tag{23}$$

It will be seen that equation (23) can be rewritten as equation (20) except that G^* is calculated using Tangren's method. The exiting fluid specific volume (v_e) is the reciprocal of the exiting

fluid density (ρ_e) and so equation (20) can be written as equation (9). Equation (9) can now be substituted into equation (8) to give an equation for the vent area, also replacing the upstream vessel pressure (P_o) with the maximum allowable pressure (P_m):

$$A = (dQ/dt)_{g,max} (\rho_e / P_m)^{1/2} (1 / G^*) \tag{24}$$

Making the homogeneous vessel assumption means that the exiting fluid density (ρ_e) is assumed to equal the vessel average density (ρ_o) which is calculated using equation (6). The vessel two phase density can also be calculated from the void fraction (α_o) and the density of the liquid phase in the reactor (ρ_f) as:

$$\rho_o = (1-\alpha_o) \rho_f \tag{25}$$

Now replacing ρ_e in equation (24) with $(1-\alpha_o) \rho_f$ from equation (25):

$$A = ((dQ/dt)_{g,max} (\rho_f / P_m)^{1/2} ((1-\alpha_o)^{1/2} / G^*) \tag{26}$$

HSL GAS-ONLY AND TWO-PHASE VENT SIZING CALCULATIONS

The results of large scale tests will be compared with DIERS gas-only and homogeneous vessel two-phase vent sizing calculations. There are a limited number of large scale tests available. It is important to consider peroxide / solvent mixtures of varying reactivities. The large scale data should include maximum pressures and vent areas for vessels of various sizes or batch masses. Adiabatic data is also needed for the same peroxide / solvent mixture using a similar external heating rate to perform the DIERS vent sizing calculation. The UN vent sizing method is based on the assumption that the ratio of the vent area to tank capacity is constant and can be determined using a reduced scale tank of 10 dm^3 capacity. Graphs will be generated for three systems showing maximum pressure versus vent area per unit volume or mass. The graphs will show experimental test data and DIERS calculated vent sizes. The three systems selected for the vent sizing comparisons are:

- 37.5% by weight of bis (3,5,5-trimethyl hexanoyl) peroxide in isododecane,
- tert-butyl peroxy-2-ethylhexanoate in isoparaffinic solvent, and
- technical pure dicumyl peroxide.

The DIERS vent sizing equations used in this analysis will be summarised here for ease of reference. The maximum rate of gas generation is calculated using equation (5). Hare's simplified gassy equation (equation 26) will be used as the homogenous vessel two-phase flow vent sizing equation. Equation (16) (Fauske's gassy equation without the assumption of that the vessel is always liquid full) will be used as the gas-only flow vent sizing equation. Note that equation (16) implies the use of equation (5) to calculate the maximum rate of gas evolution. For both homogeneous vessel two-phase and gas-only vent sizing methods backpressure corrections will be ignored but friction will be allowed for.

SYSTEM 1 - BIS (3,5,5-TRIMETHYL HEXANOYL) PEROXIDE

The first system for study is 37.5% by weight of bis (3,5,5-trimethyl hexanoyl) peroxide in isododecane. Akzo Nobel market this peroxide mixture as Trigonox 36-CD37.5 - UN No 3119. It is available either as a 900 kg IBC or portable tank. Data on this system was included in papers by de Groot et al[14,15] and Wakker and de Groot[16]. Schuurman[17] gave HSL a

tabulated summary of this data for 8.3, 9, 33 and 234 dm^3 vessels. The fill levels were 60, 80 and 90%. Schuurman[18] also provided decomposition data for the system. The major gaseous product is carbon dioxide (molecular weight 44 kg $kmol^{-1}$). The adiabatic data necessary to perform the vent sizing calculations was based on papers by Fauske[9,10,19,20,21]. Fauske performed his RSST test with an external heating rate (fire simulation) of about 0.8°C min^{-1}.

Figure 1 is a plot of maximum pressure versus vent area per unit volume (A/V). It shows experimental and calculated maximum pressures for homogeneous vessel two-phase flow and gas-only flow vent sizing. Calculated maximum pressure versus (A/V) lines are shown only for an 80% fill level.

The adiabatic data came from an RSST experiment. The RSST can only be operated as an "open system" where the test cell is connected to a much larger capacity containment vessel in which the pressure is measured. Open system tests are recommended by DIERS for gassy systems and have the advantage that effects of gas solubility in the solvent are limited. The two-phase vent sizing method, which made the homogeneous vessel assumption, would appear to be overly conservative. Gas-only flow vent sizing fits the experimental data better. The UN vent sizing method seems to be applicable to this system because experimental data from different vessel volumes lie on the same curve.

SYSTEM 2 - TERT-BUTYL PEROXY-2-ETHYLHEXANOATE

The second system for study is tert-butyl peroxy-2-ethylhexanoate in organic mineral solvent. HSL undertook some pilot plant tests using 20% by weight of this peroxy ester in an isoparafinic solvent catalysed by cobalt accelerator (Etchells *et al.*[22]). The HSL tests simulated a runaway reaction in a chemical reactor and investigated the vent size required. The reactor volume is 340 dm^3. The vent area was not varied, but tests were performed using 100, 150, 200 and 250 dm^3 batch volumes. Akzo data on 25 and 30% by weight of tert-butyl peroxy-2-ethylhexanoate in isododecane was available from Schuurman and Wakker[23] and Schuurman[24]. The 30% by weight formulation is marketed by Akzo as Trigonox 21-C30 UN No 3119 and is supplied as a portable tank. The Akzo tests were performed using 8.3 and 10.2 dm^3 vessels which are normally run 90% full. The external heating rate was the main variable.

Schuurman[18] also provided decomposition data for the system. The major gaseous product is carbon dioxide (molecular weight 44 kg $kmol^{-1}$). The adiabatic data necessary to perform the vent sizing calculations was based on HSL Phi Tec tests for the 20% by weight mixture performed with accelerator concentrations of 1% and 0%. Note that the HSL adiabatic tests were initiated at 95°C with no imposed external heating rates. Three sets of adiabatic data were available for each accelerator concentration: Closed cell- raw pressure rate; closed cell - dissolved gas corrected rate and open cell pressure rate. The pressure rates and free volumes vary between the data sets. For closed system tests, the measured pressure is reduced due to dissolved gas, therefore dissolved gas corrected pressure rates were generated.

Figures 2 and 3 are plots of maximum pressure versus vent area per unit mass (A/m_o), showing gas-only flow and homogeneous vessel two-phase flow vent sizing respectively. Vent area per unit mass is used as the X-axis because the HSL tests were performed using the same vessel but with different batch volumes. The HSL pilot tests are of interest, even though they are not fire simulations, because they show the effect of scale-up and explore the validity of the DIERS gas-only and homogeneous two-phase vent sizing methods. In Figure 3, the 1% accelerator calculations are for a fill level of 74% (the largest fill used) and the 0% accelerator calculations are for a fill level of 90%. Note: only Akzo data with low maximum pressures due to lower heating rates have been included in the figures.

Considering firstly the HSL data. Assuming gas-only flow for vent sizing was never conservative. Using homogeneous two-phase flow for vent sizing was conservative for closed

system tests provided allowance was made for dissolved gas; otherwise it was non conservative. Using homogeneous two-phase flow for vent sizing was overly conservative for open system tests. The experimental density was less than the homogeneous density; i.e. more gas and less liquid in the two-phase flow. Using the experimental density rather than the homogeneous density, a better prediction of the experimental mass flux was achieved. The flow regime seemed to be bubbly rather than homogeneous. The UN vent method does not appear to be applicable to this system.

Considering secondly the Akzo data. Adiabatic data was not available for the external heating rates used in the Akzo experiments, whereas the HSL adiabatic tests were performed without external heating. Thus for the 30% peroxyester tests, most of the predicted maximum pressures for homogeneous two-phase flow fell below the experimental values, apart from those based on open cell data. This shows the importance of performing an adiabatic test with the same external heating rate as used in the experiment. The other factor was the differences in peroxide concentration and the choice of solvent. This shows the importance of performing an adiabatic test using the same reaction mixture as used in the experiment.

SYSTEM 3 - NEAT DICUMYL PEROXIDE.
The third system for study is dicumyl peroxide. This system is of interest because of the incident at Calhoun in 1990 involving 1.7 m^3 (450 US gallon) tanks (NTSB[25]). Hercules, whose chemical (Di-Cup 99 wt% solid UN 3109 type F solid) and tanks (DOT spec 57) were involved in the incident, later carried out some tests using 0.22 m^3 (58 US gallon) tanks (Gove[26]) with an external heating rate of 0.8 °C min^{-1}. Later the Organic Peroxide Producers Safety Division (OPPSD) had some 10 dm^3 tests carried out at a variety of external heating rates between 2 and 9°C min^{-1} (Plowright[27]). Finally OPPSD carried out a fire engulfment tests on a 1.74 m^3 (460 US gall) tank (McCloskey[28] and Coffey[29]). For this test the equivalent heating rate was calculated to be 6°C min^{-1}. Schuurman[18] also provided decomposition data for the system. The major gaseous product is methane (molecular weight 16 kg kmol^{-1}). The adiabatic data necessary to perform the vent sizing calculations was based on papers by Fauske[9,10,19,20,21]. Fauske performed his RSST test with an external heating rate (fire simulation) of about 1°C min^{-1}.

Figure 4 is a plot of maximum pressure versus vent area per unit volume (A/V). It shows experimental and calculated maximum pressures for homogeneous vessel two-phase flow and gas-only flow vent sizing. Calculated maximum pressure versus (A/V) lines are shown only for an 80% fill level.

Gas-only flow vent sizing calculations fit reasonably with the 58 US gall tests (0.8°C min^{-1}), and the OPPSD 10 dm^3 (2°C min^{-1}) and 1.74 m^3 (460 US gall) (6°C min^{-1}) tests. However tests on vessels with higher external heating rates show much higher pressures. This shows the necessity of performing an adiabatic test with the same external heating rate. Homogeneous two-phase vent sizing was overly conservative. The OPPSD 10 dm^3 tests used a high heating rate of 9°C min^{-1} and so cannot really be compared with the calculated vent sizes. Fauske[19] thought that the reaction mechanism changed from homogeneous to propagating. The UN vent sizing method would appear to be applicable to this system.

DISCUSSION

UN VENT SIZING METHOD

The initial test proposal assumed a heat load of 110 kW m^{-2}. This is typical of the heat flux usually given for open pool fires. However much higher heat fluxes are possible with jet fires (250 to 300 kW m^{-2}). The current UN method uses a heat load calculation method consistent with API 520. This results in a significantly lower heat load than would be produced using 110 kW m^{-2}. Thus the external heating applied to the test vessel, used to simulate fire engulfment, may not be adequate. Assuming that only pool fires are conceivable as the external heat flux is not conservative. The Calhoun incident showed that large fireballs can be generated on a trailer carrying a number of IBCs. Also jet fires could occur when the portable tank is being loaded or unloaded at the chemical plant rather than on the road. Only the tank surface below the liquid level is heated. This is not the worst case.

FUNDAMENTALS OF DIERS VENT SIZING

DIERS vent sizing methods are for the maximum gas generation rate, which is the worst case for gassy systems. Homogeneous two-phase flow is the worst case and this was the basis of the early DIERS work. It was recognised that this can be overly conservative and therefore DIERS gas only flow methods have been developed. Care needs to be taken however in assuming that no liquid carry over occurs. A small amount of liquid carry over (much less than the homogeneous vessel assumption) can cause a larger vent to be required. Assuming gas only flow would then produce an undersized vent.

DISCUSSION OF HSL VENT SIZING CALCULATIONS

The intention here was to compare the available experimental data with vent sizing calculations performed using the DIERS gas-only and homogeneous two-phase flow vent sizing methods. Note that there is only a limited amount of experimental data available. One particular problem was obtaining reliable adiabatic data for the same peroxide concentration with a comparable external heating rate.

- For system 1 (3,5,5-trimethyl hexanoyl peroxide) DIERS gas-only flow vent sizing and the UN method both seemed applicable.
- For system 2 (tert-butyl peroxy ethyl hexanoate) the experimental HSL data indicated a bubbly two-phase venting mixture. The DIERS gas-only flow vent sizing and UN methods were shown not to be safe. DIERS homogeneous two-phase vent sizing was shown to be conservative provided either open system test data or closed system dissolved gas corrected data was used. A fair vent sizing comparison could not be made with the Akzo data because adiabatic data was not available with the higher peroxide concentration, the different solvent and the variety of external heating rates.
- For system 3 (dicumyl peroxide), some tests with low external heating rates and larger vessels seemed to fit the DIERS gas-only flow vent sizing and UN methods. A fair vent sizing comparison could not be done with tests using high external heating rates because of the lack of adiabatic data.

Two-phase flow is caused by liquid level swell. If the level swell is low, then gas-only flow occurs. In practice, the vent flow is often two-phase but with a lower density than predicted by the homogeneous vessel assumption. For accurate vent sizing, if two phase flow occurs, a method is required to calculate the actual density (not the homogeneous density) and therefore the mass flux of the venting mixture. However if gas only flow is predicted, it is important to know the molecular weight of the gas products and this is not always easy to determine. For the gas evolution rate calculation, closed cell tests are affected by gas

solubility if there is a solvent present and this causes problems if the intended maximum pressure is lower than the test cell pressure at the maximum pressure rate. For open cell tests a temperature correction should be made.

The HSL validation work was only able to consider a limited number of large scale tests because of the lack of published data. System 1 is the most commonly quoted example of the validity of the UN vent sizing approach. A range of systems needs to be considered to show the general validity of the UN method.

CONCLUSIONS

There may be potential problems with how the UN method assesses the effect of heat flux on the venting and decomposition of the organic peroxide as it only considers pool fires and only the wetted surface of the tank is used to calculate the heat transfer.

Only a limited amount of reliable validation has been possible in terms of comparisons with the DIERS vent sizing methods. For those experimental data available, the UN test was conservative for two cases but non-conservative for one case. However to make definitive conclusions would require considerably more experimental data.

The UN vents sizing method may not be valid in all peroxide venting cases and other methodology may need to be developed. The UN method would seem to be applicable to largely gas-only flow venting. If there were a significant amount of two-phase flow then the DIERS homogeneous method would seem to be applicable. The problem arises for intermediate cases where there is a low liquid fraction two-phase flow. Here the UN method would not be safe and the DIERS homogeneous method would be overly conservative. Again to make definitive conclusions would require considerably more experimental data.

NOMENCLATURE

A	Vent area, m^2
A_w	Wetted area, m^2
A_p	Portable tank vent area, m^2
A_t	Test vessel vent area, m^2
C_D	Discharge coefficient (assumed to be 1.0 for this analysis)
F	Insulation factor
G	(Two-phase) mass flux, $kg\ m^{-2}\ s^{-1}$
G	Mass flux, $kg\ m^{-2}\ s^{-1}$
G^*	Dimensionless mass flux
K	Heat conductivity of insulation layer, $W\ m^{-1}\ K^{-1}$
k	Isentropic coefficient
L	Thickness of insulation layer, m
M_W	Molecular weight of gas, $kg\ kmol^{-1}$
m_o	Reaction mass, kg
m_t	Test sample mass, kg
P_m	Maximum allowable pressure, Pa
P_o	Upstream vessel pressure, Pa
P	Pressure, Pa
$(dP/dt)_{max}$	Maximum pressure rate, $Pa\ s^{-1}$
q	Heat absorption, W
$(dQ/dt)_{g,max}$	Maximum rate of gas evolution, $m^3\ s^{-1}$
R	Gas constant $= 8314\ J\ kmol^{-1}\ K^{-1}$
T_{PO}	Temperature of the peroxide at the relieving conditions, K
T	Temperature, K

T_t	Temperature in test cell, K
T_c	Temperature in containment volume, K
U	Heat transfer coefficient of the insulation (K/L), W m^{-2} K^{-1}
V	Reactor vessel volume, m^3
V_f	Free volume (either test cell free space (closed cell) or containment volume (open cell)), m^3
V_p	Portable tank volume, m^3
V_t	Test vessel volume, m^3
v_e	Exiting fluid specific volume, m^3 kg^{-1}
W	Vent mass flow rate, kg s^{-1}
α_o	Void fraction
ρ_e	Exiting fluid density, kg m^{-3}
ρ_g	Gas density, kg m^{-3}
α_o	Void fraction
ρ_o	Vessel two phase density, kg m^{-3}
ρ_f	Liquid (reactant) density, kg m^{-3}
η_c	Critical pressure ratio
η	Pressure ratio
ω	Omega, dimensionless number

ACKNOWLEDGEMENTS

REFERENCES

1.   Fisher HG et al, "Emergency relief system design using DIERS technology - The DIERS project manual", AIChE, New York, 1992
2.   United Nations, "Recommendations on the transport of dangerous goods - Manual of Tests and Criteria", 3rd revised edition, United Nations, Geneva, 1999
3.   ECE, "European agreement concerning the international carriage of dangerous goods by road (ADR) and protocol of signature", United Nations, Geneva, 1998 and 2001
4.   ECE, "European agreement concerning the international carriage of dangerous goods by rail (RID) and protocol of signature", United Nations, Geneva, 1998 and 2001
5.   United Nations, "Recommendations on the transport of dangerous goods - Model regulations", 11th revised edition, United Nations, Geneva, 1999
6.   American Petroleum Institute (API), Recommended Practice RP520, Part 1 1993
7.   Leung JC, "Chemical process relief system design seminar" held at Decines, France, September 1998.
8.   Leung JC, "The Omega method for discharge rate calculations", International Symposium on Runaway Reactions and Pressure Relief Design, Boston, August 1995.
9.   Fauske HK, "The reactive system screening tool (RSST): An easy inexpensive approach to the DIERS procedure", Process Safety Progress, Vol 17, No 3, p190-195, Fall 1998.

10.   Fauske HK, "The reactive system screening tool (RSST): An easy inexpensive approach to the DIERS procedure", International Symposium on Runaway Reactions, Pressure Relief Design and Effluent Handling, New Orleans, March 1998.

11.   Etchells J and Wilday J, "Workbook for chemical reactor relief system sizing", HSE Contract Research Report, 136/1998, 1998

12.   Tangren RF, Dodge CH and Seifert J, Journal of Applied Physics, Vol 20, No 7, p637-645, 1949.

13.   Leung JC and Fauske HK, "Runaway system characterisation and vent sizing based on DIERS methodology", Plant Operations Progress, Vol 6, No 2, p77-83, April 1987

14.   de Groot JJ, Groothuizen ThM and Verhoeff J, "Relief venting of thermal explosions", Loss Prevention and Safety Promotion in the Process Industries, 3rd International Symposium, Basle, Vol 3, p13/944-13/955, September 1980.

15.   de Groot JJ, Groothuizen ThM and Verhoeff J, "Safety aspects of organic peroxides in bulk tanks", Industrial and Engineering Chemistry, Process Design and Development, Vol 20, p131-138, 1981.

16.   Wakker JP and de Groot JJ, "Venting of decompositions of energetic liquids using a bottom vent", Process Plant Safety, Symposium Proceedings, AIChE, Vol 2, p55-71, 1996.

17.   Schuurman P, "Bulk experiments Bis (3,5,5-trimethyl hexanoyl) peroxide 37.5% w/w in isododecane", private communication to HSL, September 1996.

18.   Schuurman P, "Akzo Nobel: Technical bulletins on thermal decomposition mechanisms on Trigonox 21, Trigonox 36 and Perkadox BC", private communication to HSL, April 2000

19.   Fauske HK, "The RSST provides pressure relief requirements for organic peroxides", FAI Process Safety News, Spring 1998.

20.   Fauske HK, "Advances in relief system design", 22nd US DIERS Users Group Meeting, Charleston, October 1998.

21.   Fauske HK, "Advances in chemical reaction hazard evaluation: Prevention and accommodation", 23rd US DIERS Users Group Meeting, Las Vegas, April 1999.

22.   Etchells JC, Snee TJ and Wilday AJ, "Relief system sizing for exothermic runaway: The UK Strategy", International Symposium on Runaway Reactions, Pressure Relief Design, and Effluent Handling (New Orleans), AIChE, p135-162, March 1998.

23.   Schuurman P and Wakker JP, "Emergency relief sizing of organic peroxide tank - container by venting tests", OECD-IGUS EOS meeting, Boston, March 1994

24.   Schuuram P, "Trigonox 21 = tert.butylperoxy-2-ethylhexanoate = Tx21", private communication to HSL, March 2000

25.   National Transportation Safety Board (NTSB), Highway Accident Report "Multiple-vehicle collisions and fire during limited visibility (fog) on Interstate 57 near Calhoun, Tennessee, December 11, 1990", PB92-916202, NTSB/HAR-92/02, 1992

26.   Gove SH, "Emergency pressure relief for intermediate bulk containers containing dicumyl peroxide - Incident report and test data", 18th US DIERS Users Group Meeting, Houston, February 1996.

27.   Plowright JD, "Thermal decomposition testing of organic peroxides: New 10 litre test data", OECD-IGUS EOS Meeting, Stockholm, May 1999.

28.   McCloskey C, "Fire engulfment test of an IBC filled with dicumyl peroxide",OECD-IGUS EOS Meeting, Buxton, December 1999.

29.   Coffey MV, "Emergency venting testing", OECD-IGUS EOS Meeting, Buxton, April 2000
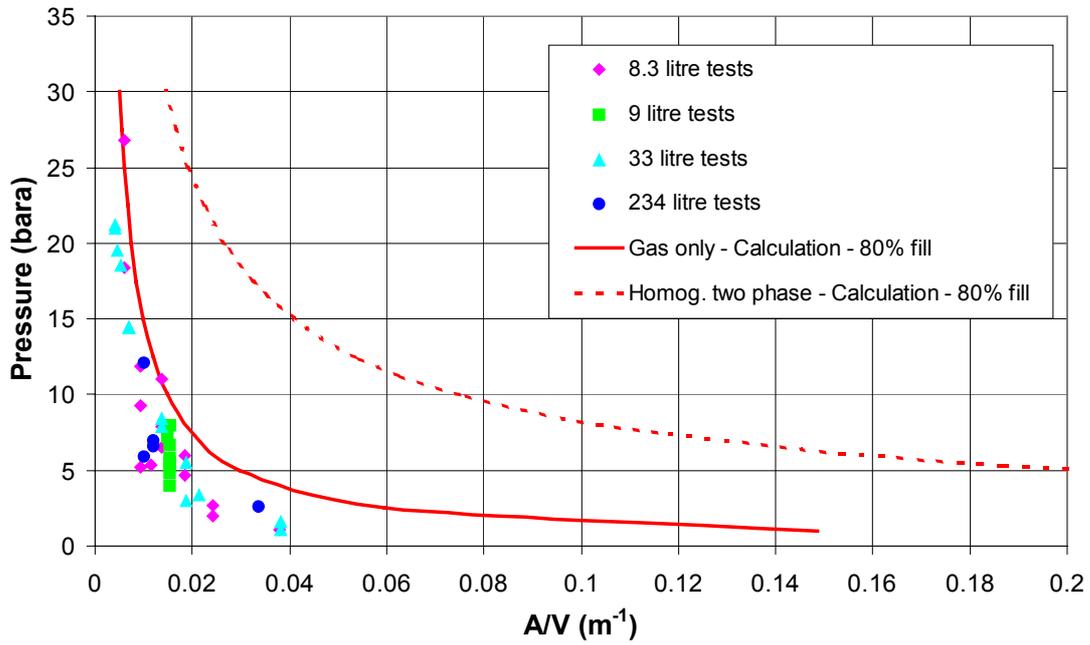
Figure 1. Bis (3,5,5-trimethyl hexanoyl) peroxide (37.5% w/w) in isododecane
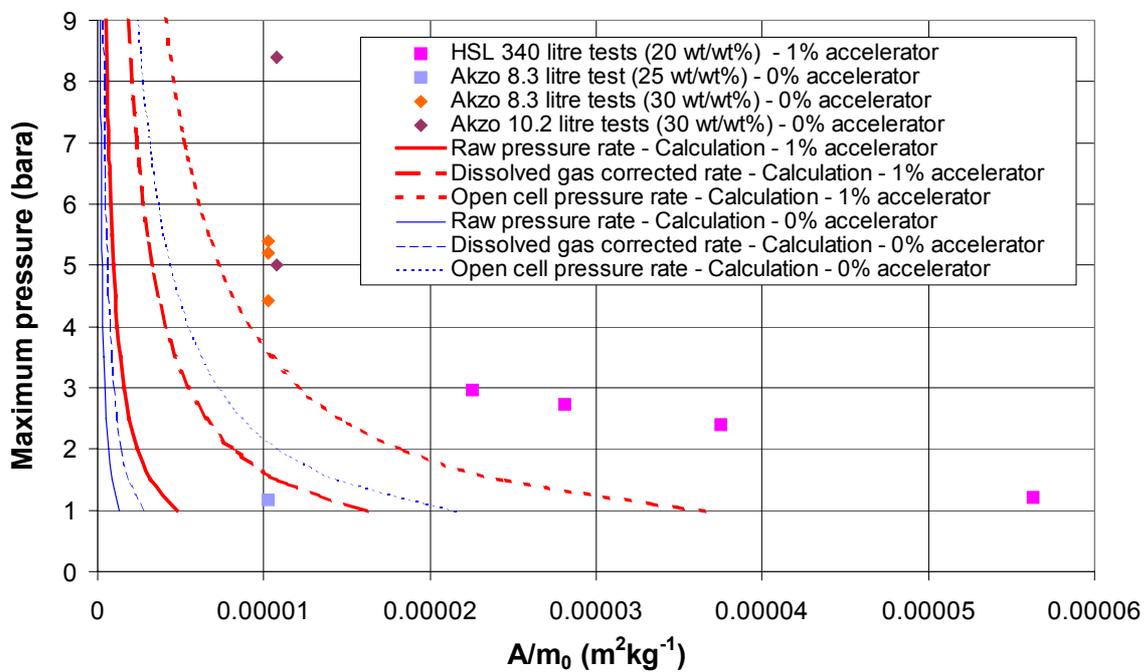
Figure 2. Peroxyester in solvent (Gas only flow)
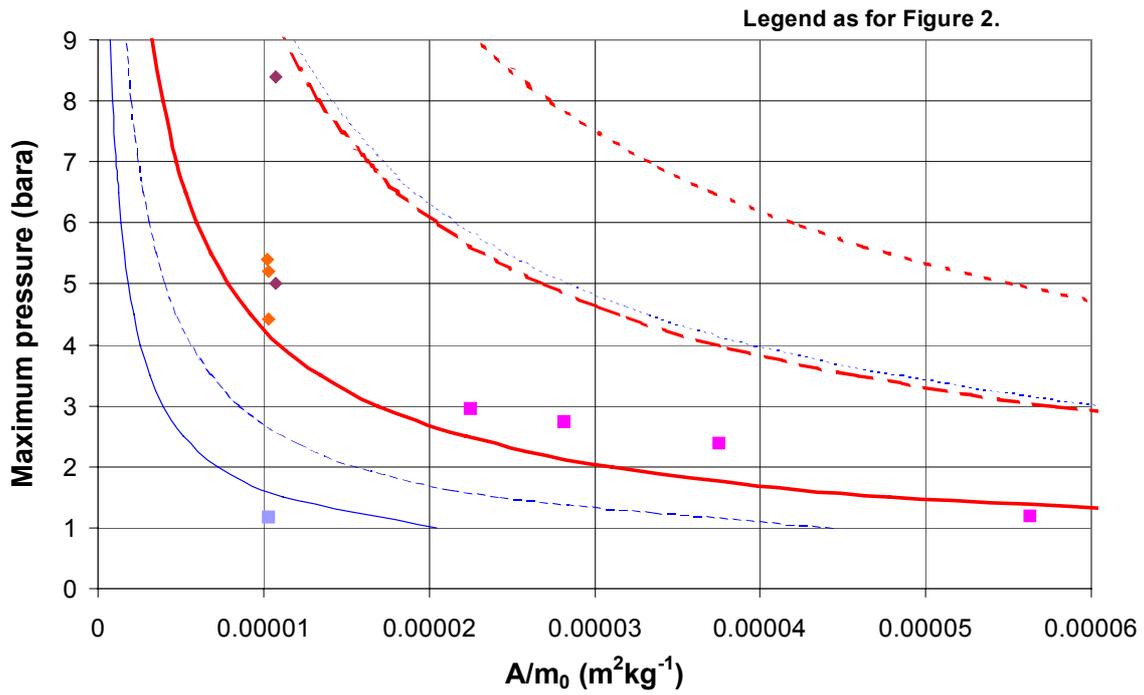
Figure 3. Peroxyester in solvent (Homogeneous two-phase flow)
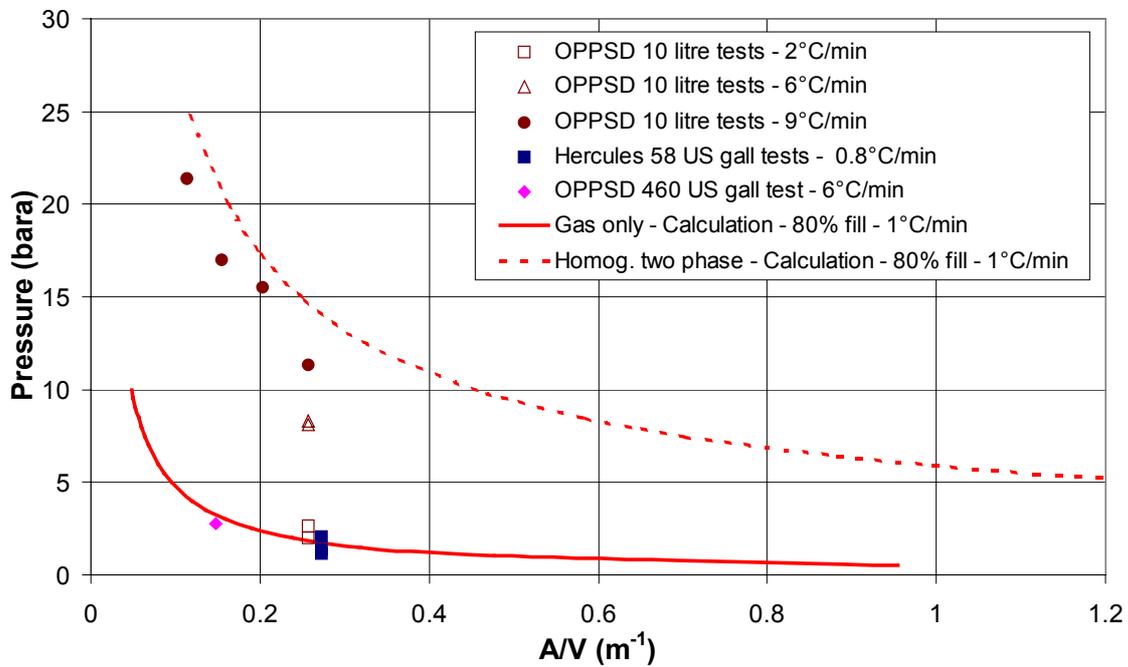
Figure 4. Dicumyl peroxide