RELIEF SIZING FOR DECOMPOSITION REACTIONS : IMPROVED METHODOLOGY

Dr Jasbir Singh

Hazard Evaluation Laboratory Ltd, Barnet, Herts EN5 5TS

Process equipment in which exothermic runaway reactions might occur, are normally protected by a relief vent which should protect the vessel against overpressurization. When relief is actuated, the vented fluid is often a complex mixture of gas/vapour and liquid and the vent sizing must take full account of this. This paper discusses a new method for sizing vents when the reaction generates a non-condensible gas. The method is a major improvement on the traditional DIERS methodology, leading to much smaller but still safe vents.

Venting, Exothermic reactions, DIERS, reactors, safety, relief

1. INTRODUCTION

It is not uncommon to encounter materials in the fine chemicals industry that are prone to gas generation while undergoing exothermic decomposition at elevated temperature. Gas generation is not limited to decomposition but can also be the by-product of chemical reactions. In either case, the pressure generated (in a closed vessel) and the rate of pressure rise can by very high, certainly much greater than the vapour pressure of the liquid reactants or products. This has important implications when a reacting system of this type has to be vented for safety reasons.

In such a case, when the gas is relieved through the vent, the temperature of the reactants continues to rise because relief of the gas produces no liquid cooling. If there was a significant vapour content the situation would be much better since cooling would result by virtue of the latent heat associated with the vapour. Another aspect of chemical reaction

relief is that when a vent opens, the relieved fluid is often a two-phase mixture of the gas and liquid. The presence of liquid in the vent line reduces the space available for the gas and in general leads to the need for larger vents.

A simple method for calculating the relief area A, which will safely protect a vessel of volume V_o containing m_r reactant, from exceeding a pressure P_m is given by (ref. 1):

$$A = \frac{m_r^2 \; V_e \; T_r}{G \; m_e \; V_o \; T_e \; P_m} \left(\frac{dP}{dt}\right)_{max,e} \qquad (1)$$

This was proposed by DIERS and is based on the assumption that two-phase flow (with mass flux G) occurs at the highest pressure rise rate. The variables V_e, T_r, M_e, T_e and $(dP/dt)_{max,e}$ are experimental parameters which characterize the exotherm. In fact the maximum gas generation rate Q_g is given by,

$$Q_g \approx \frac{V_e}{P_m} \frac{T_r}{T_e} \left(\frac{dP}{dt}\right)_{max,e}$$

where V_e is the volume of gas space in the experimental equipment, T_e its temperature and T_r the reactant temperature at the maximum rate of pressure rise $(dP/dt)_{max,e}$.

The above equation represents a significant simplification of the vent sizing problem and although it gives safe results the actual relief area predicted is extremely large. This frequently presents a problem because the large relief sizes predicted cannot be accommodated on reactor vessels.

2. MATHEMATICAL DESCRIPTION OF DECOMPOSITION REACTION RELIEF

2.1 RIGOROUS EQUATIONS

The experimental data typically used in equation (1) may be derived from an adiabatic calorimeter such as PHI-TEC II. A sketch of the experimental set-up is shown in figure 1 (ref 2). This shows an adiabatic calorimeter in which the test sample (of mass m_e) is allowed to undergo chemical reaction without heat loss. This is achieved by placing the sample within a set of guard heaters; the temperature of the heaters is controlled to match that of the sample as the exotherm proceeds. Any gas which is generated by the reaction expands into a space of volume V_e, this being the volume of the containment vessel. Another important feature is that the test cell is made from very thin metal so that its thermal mass is negligible compared with that of the chemical sample.

The commercial vessel for which the vent is to by sized is shown in figure 2, together with the important variables needed.

With the information from the experimental apparatus in figure 1, it is possible to describe the pressure-time relationship in a full-scale vessel where the exothermic reaction may be

taking place. The governing equation for the rate of pressure rise in a closed vessel, $(dP/dt)_c$, is (ref 3):

$$\left(\frac{dP}{dt}\right)_c = \left(\frac{M_r}{M_e}\right)\left(\frac{V_e}{V_g}\right)\left(\frac{1}{T_e}\right)\left\{T_r\left(\frac{dP}{dt}\right)_e + (P - P_i)_e \frac{dT_r}{dt}\right\} \qquad (2)$$

The variables with the subscript 'e' are test dependent, the others are either 'fundamental' to the reaction or determined by the full scale reactor facility.

If the vessel in which the runaway is taking place is fitted with a vent which opens at time t_v when the relief set pressure P_v is reached, the pressure-time relationship in the vented vessel may be obtained from:

$$\left(\frac{dP}{dt}\right)_v = \left(\frac{dP}{dt}\right)_c \frac{1}{m_r}\left(m_r - F\,(1 - x)\,(t - t_v)\right) - \frac{P}{V_g} F \nu \qquad (3)$$

where F is the venting rate corresponding to the assumed relief area, V_g is the gas space in the reactor, υ the two-phase specific volume leaving the reactor and x the mass fraction of gas in the vented fluid mixture.

The above equations can be used to obtain a complete understanding of the venting incident and the influence of important engineering variables.

2.2 SIMPLIFIED ANALYTICAL SOLUTION

It is possible to simplify equation (3) to give an analytical solution for the vent area A:

$$A = \frac{m_r^2\, V_e\, T_r}{G\, m_e\, V_o\, T_e\, P_m\, K}\left(\frac{dP}{dt}\right)_{max,e} \qquad (4)$$

where K is a correction factor

$$K = 1 + \frac{2\left[1 - (dP/dt)_v / (dP/dt)_m\right]}{\left[1 + (dP/dt)_v / (dP/dt)_m\right]}$$

Comparing equation (4) with the DIERS equation (1), the vent area is reduced by the factor K. This means that when $(dP/dt)_v \ll (dP/dt)_m$ the relief area is a factor 3 smaller than that predicted by DIERS. When $(dP/dt)_v \simeq (dP/dt)_m$, equation (4) reduces exactly to equation (1). The parameter G in the relief sizing equations is the mass flux for two-phase flow; for gassy reactions this is a function only of pressure and void fraction and may be calculated from the simple equations given in ref 4.

3. APPLICATION TO RUNAWAY REACTION

3.1 COMPARISON WITH DIERS EQUATION

The simplified analytical equation was applied to a hypothetical reactor vessel with the following properties:

- reactor volume = 5 m^3, cross-sectional area 1 m^2
- relief set pressure = 3, 10 or 20 bara
- reactant density 1000 kg/m^3

The decomposition reaction data used for the assessment is shown in figures 3 and 4 The rise in pressure and temperature (as measured experimentally) is shown in figure 3 and the rate of pressure rise, as a function of reactant temperature, is shown in figure 4.

The results for the vent sizes are given in figure 5, where the relief area predicted by the DIERS equation is compared with the new analytical equation (4) for three different relief opening pressures. These calculations are based on the assumption of a foamy liquid, resulting in the relief of a two-phase gas-liquid mixture.

3.2 COMPARISON OF DETAILED AND ANALYTICAL EQUATIONS

For the same reactor system as above, the data from the detailed evaluation, equation (3), is compared with equation (4) in figure 6. This shows that although equation (4) gives areas much smaller than the DIERS equation, the detailed evaluation reveals that even equation (4) is quite conservative. This is true except at very low void fractions, where the two methods converge. At low void fraction, the DIERS equation also agrees with equations (3) and (4).

3.3 EFFECT OF VAPOUR-LIQUID DISENGAGEMENT

When applying equation (4), the assumption is that two-phase flow commences when $(dP/dt)_v$ is reached, this being the rate of pressure rise at the relief set pressure. In equation (3), two-phase flow begins when the pressure P_v is reached.

An important parameter to consider is the possibility of a delay in two-phase flow onset. This will potentially increase the mass of reactants present in the rector when the worst (highest) dP/dt is reached and could therefore increase the relief size needed for a given overpressure. One practical way in which two-phase flow initiation can be delayed is if the liquid does not foam but rather is carried over as a result of the high velocity generated during relief. The churn-turbulent model (ref 5) is often used to evaluate the gas rate which will lead to liquid carry-over.

The results of several calculations using the reactor system described above are given in figure 7, comparing the effect of a foamy system with a churn-turbulent one. (In both cases, the calculations were performed using the detailed calculation model, equation 3). For the system considered here, the relief area needed for a churn-turbulent system is a factor 1.8 to 2 higher than for a foamy system (for the same overpressure).

The reason for this difference becomes apparent in figure 8, where the mass of reactants after

relief actuation is compared for foamy and churn-turbulent system for one particular case. It is clear that mass depletion due to two-phase venting is much faster in the case of a foamy system and therefore, at any given time, the gas generation will be correspondingly smaller. If the maximum pressure is fixed, the relief area needed for the churn-turbulent case will therefore be larger.

3.4 EFFECT OF INITIAL REACTOR CHARGE

3.4.1 Foamy Systems

The quantity of reactants in the reaction vessel at the start of the runaway is commonly considered to be very important in determining the relief size. In the case of gassy reactions, the relationship between these two variables is rather complicated and it is very difficult to make any general comments. The results for a number of calculations are plotted in figure 7, discussed earlier, where churn-turbulent and foamy systems were compared. It is clear that there is no simple trend for the foamy system.

The reason for this complexity can at least partially be explained by reference to figures 9 and 10, where changes in reactor pressure and reactant mass are plotted as a function of time, following relief actuation.

It is clear that the maximum pressure, in all cases, occurs at about 75.3 to 75.5 minutes after the start of the exotherm. At this point in time (see figure 10) the mass of charge in the vessel is the same for all four cases. Compare for example $\alpha = 90\%$ and $\alpha = 20\%$ (i.e. a vessel initially only 10% full and one which is 80% full).

Surprisingly the $\alpha = 90\%$ gives the highest pressure (see figure 9). The reason is that in this instance the vent does not in fact open until $\sim$ 75.2 minutes into the runaway (i.e. quite close to worst condition); at this time, the pressure with $\alpha = 20\%$ vessel is about 2.25 bar (i.e about 0.75 bar lower). Therefore when these two vessels reach the worst condition ($\sim$75.3 to 75.4 minutes) the vessel which started with less contents in fact reaches a higher maximum pressure.

It should be understood that these precise results are specific to the relief size, relief opening pressure, vessel size, reaction kinetics etc considered here. The important point is that the results are not the same as might be expected intuitively but can logically be explained by detailed analysis.

3.4.2 Churn-turbulent systems

In situations where vapour-liquid separation can occur, the behaviour is somewhat simpler but here too, generalisations are not always possible.

From figure 7, it is clear that for the cases studied, the results are quite insensitive to initial charge. This behaviour might be observed quite frequently and the reason becomes apparent from figure 8, where mass depletion after vent actuation is presented as a function of time. In the case of the churn-turbulent system, note that the mass becomes almost constant at about 75.2 minutes after the runaway. The reason for this plateau is that the liquid level in the vessel is so low that a switch from two-phase to all-gas flow has taken place (as predicted by the churn-turbulent model).

The same result will be obtained for all 3 churn-turbulent cases studied. Therefore, the reactor will contain the same amount of reactant as the worst condition (in terms of dP/dt) is approached and so the same result will be observed. Note that although two-phase flow occurs for the systems considered, single (gas-phase) venting occurs at the critical (highest) dP/dt and so gas-phase venting actually governs the vent size.

The above observation will hold true when the initial charge is equal to or greater than the level at which two-phase flow ceases. If the initial level is lower than this critical amount, then the results will vary with the reactor charge. A lower charge (high α) will require lower vent sizes (for a fixed overpressure).

3.5 SENSITIVITY OF RESULTS

A feature that appears to be rather strange is the very sharp increase in reactor overpressure for a relatively small reduction in relief area. This is especially true for the foamy systems and this is apparent in figure 6.

This observation can be explained by recalling that the important factor is the quantity of reactant at the point of highest dP/dt. This mass say m_c, is given by

$$m_c = m_o - m_v$$
$$= m_o - \overline{G}\, A\, \Delta t_c$$

where m_v is the amount of reactant vented over a time Δt_c, being the time from relief opening to the time when maximum dP/dt is reached, $\overline{G}$ is the average mass flux over Δt_c and A is the relief area. For a given system, $\Delta t_c \sim$ constant and $\overline{G}$ will be reasonably constant too.

For the systems considered here, $m_c \sim 400$ kg (see figure 9, the mass at time $\sim$ 75.3 minutes); since $m_o = 4000$ kg therefore m_v is about 3600 kg. If the relief area is reduced by just 20%, then $m_v \sim 2880$ kg and so $m_c \sim 1120$ kg. The increase in m_c, by a factor of almost 3 will cause a corresponding increase in the pressure. This explains the reason for the very sharp increase in overpressure with relatively small reductions in relief area.

This behaviour will not occur if m_c is relatively large compared with m_v (instead of the reverse being true). This would be the case for example if the relief set pressure is much higher than 3 bar so that the vent opens later, closer to the maximum dP/dt. In this case a small change in relief area will not have such a dramatic effect on m_c, the mass in the reactor when the highest dP/dt is reached.

4. CONCLUSIONS

The relief sizing approach discussed in this paper represents a relatively simple but very powerful method for the sizing of vents to protect process equipment against a gas generating

exothermic runaway reaction. From a practical viewpoint, the simple analytical equation and the comprehensive simulation method, both predict vent sizes much smaller than the presently available (DIERS) method. The simulation method in addition allows detailed consideration of many engineering variables, thus giving a full understanding of the relief event and allowing designs to be optimized.

5. REFERENCES

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FIGURE 1 ARRANGEMENT OF TEST APPARATUS FOR GASSY REACTION TEST

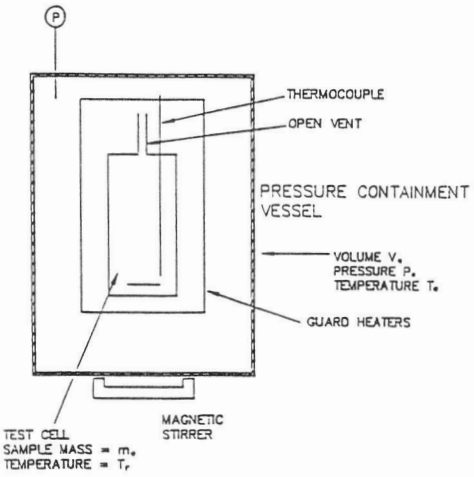

FIGURE 2: MAIN VARIABLES IN GASSY REACTION MODEL

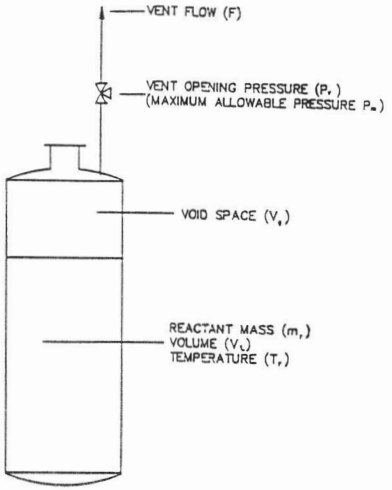

FIG 3 RUNAWAY REACTION - EXPERIMENTAL DATA
PRESSURE & TEMPERATURE Vs TIME

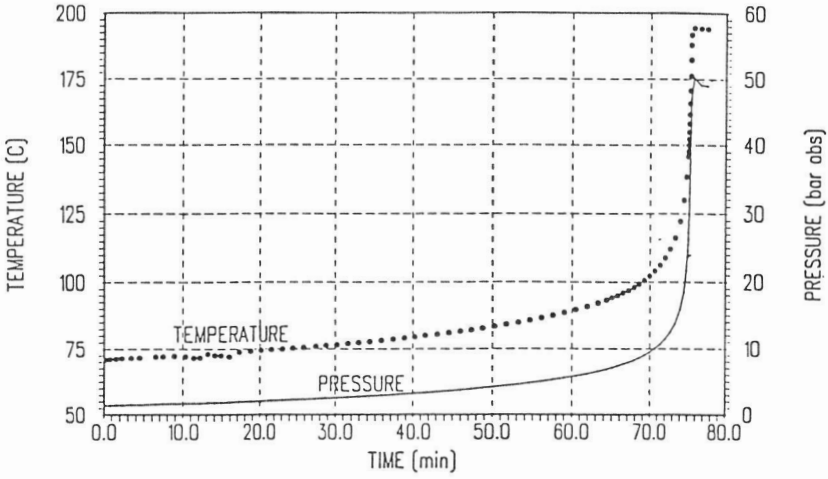

FIG 4 : RUNAWAY REACTION EXPERIMENTAL DATA
RATE OF PRESSURE RISE Vs TEMPERATURE

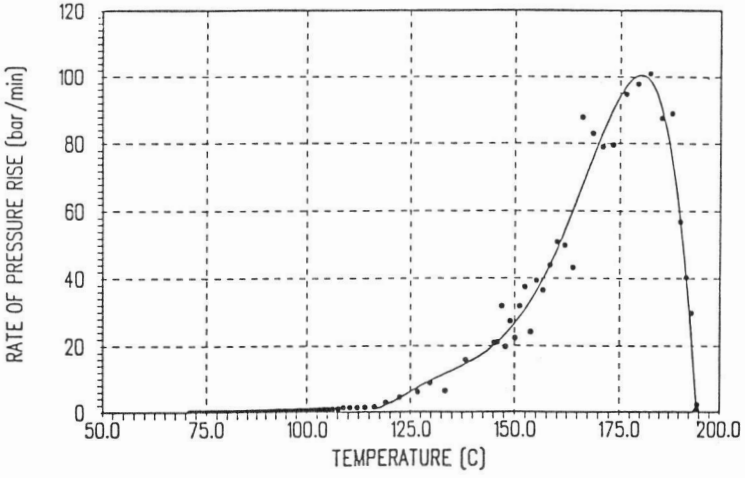

FIG 5. VENT AREA RATIO Vs REACTOR VOID FRACTION

FOAMY SYSTEM (two-phase relief)

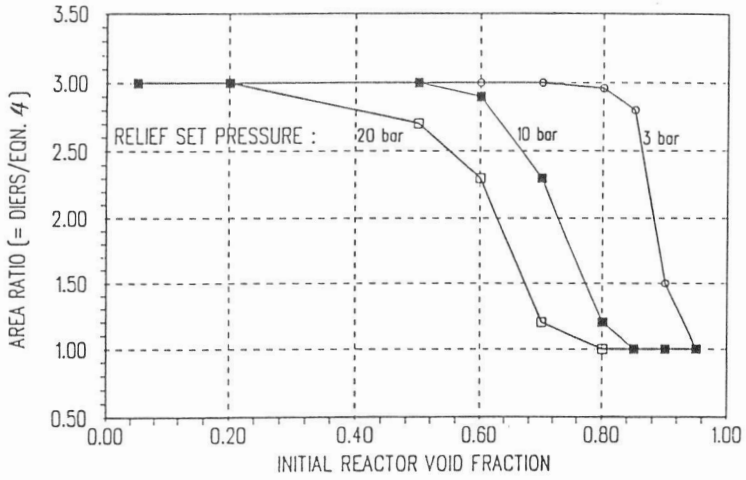

FIG 6 : COMPARISON OF SIMPLE & DETAILED METHODS

RUPTURE DISC SIZE FOR (FOAMY) TWO-PHASE RELIEF

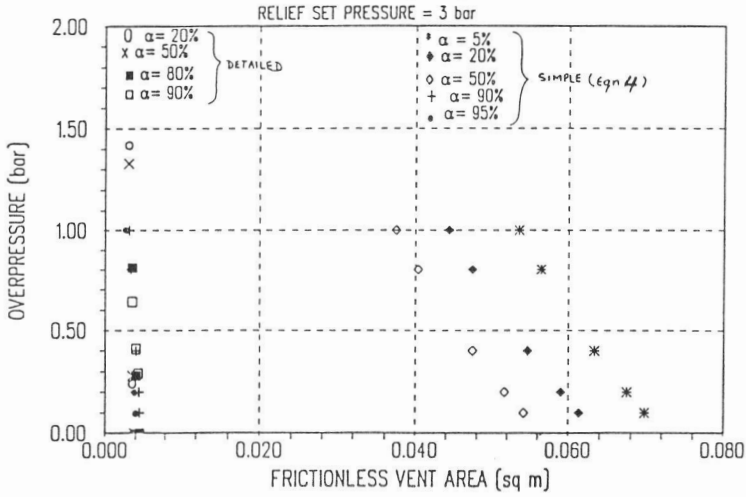

FIG 7 : RELIEF AREA CALCULATED BY DETAILED METHOD

Comparison of Foamy and Churn-turbulent Models

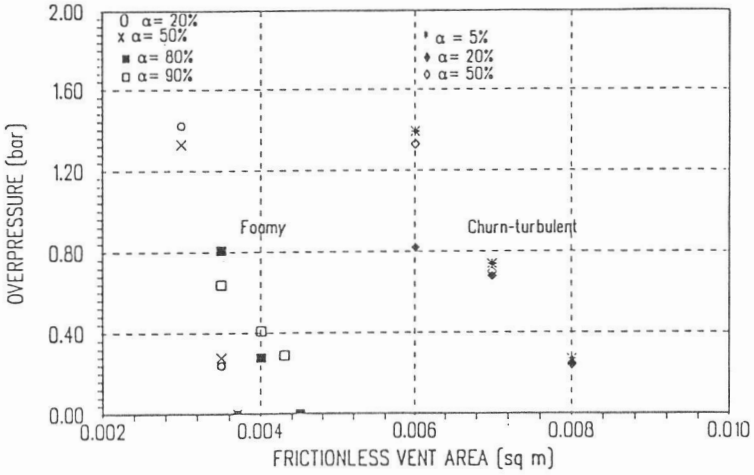

FIG 8 : MASS DEPLETION FOLLOWING RELIEF

COMPARISON OF FOAMY AND CHURN-TURBULENT SYSTEMS

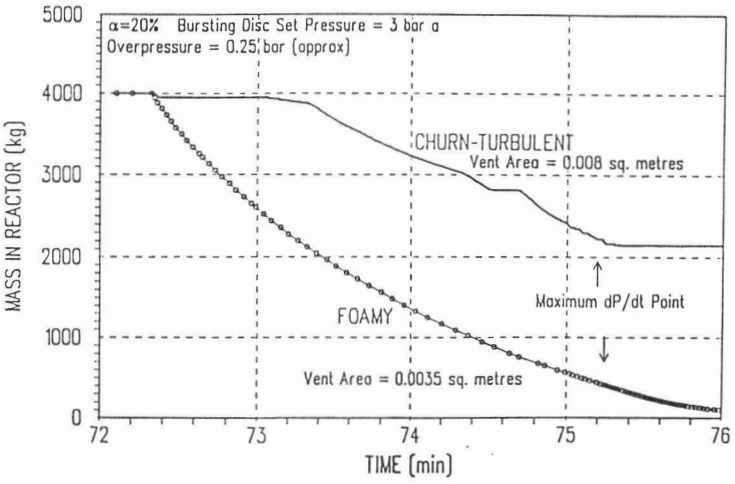

FIG 9 · EFFECT OF INITIAL VOID FRACTION ON PRESSURE CHANGE FOLLOWING VENTING

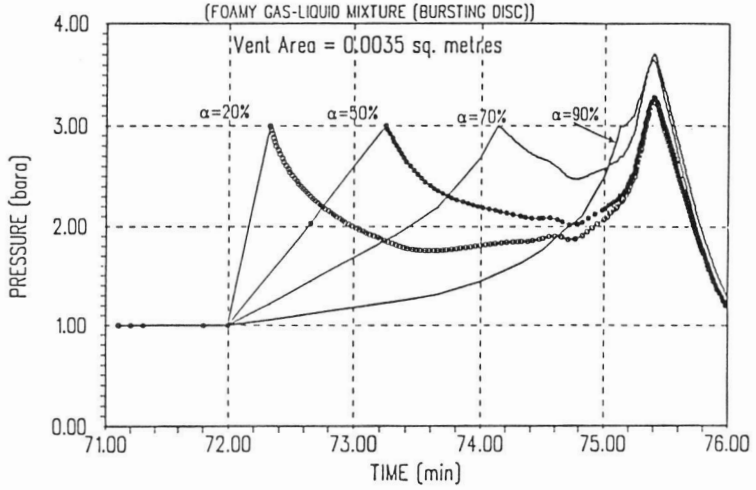

FIG 10 : EFFECT OF INITIAL VOID FRACTION ON REACTANT MASS CHANGE FOLLOWING VENTING