



Runaway reaction hazard and venting of a cyanide reaction

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The runaway reaction hazard of a cyanide reaction initiated by an amine and caustic has been studied extensively and a venting strategy formulated from the data. The relief size necessary to safely relieve such a reaction has been calculated using thermal runaway data for a number of different situations, allowing for two-phase flow.

(Keywords: runaway reactions, explosion venting, calorimeter)

This paper is concerned with the investigation of an industrial system in which the potential for complex runaway reaction explosion exists. The normal reaction is carried out in a batch reactor, operating at atmospheric temperature. The process involves two sequential steps:

Amine + formaldehyde \rightarrow intermediate

Intermediate + 'cyanide' \rightarrow product

Both of these reactions are mildly exothermic and the reactor is fitted with cooling coils to maintain temperature control. Loss of cooling or other such problems will not produce a rapid explosion. An operator error could, however, result in the cyanide and formaldehyde being added in the first step without any amine, producing no reaction:

'Cyanide' + formaldehyde \rightarrow NO REACTION

At this point, the operator may realize the error since he will observe no heat generation. In his attempt to remedy the situation, he may then add the amine, inadvertently producing a runaway explosion:

'Cyanide' + formaldehyde + amine \rightarrow runaway explosion

The objective of the work reported in this paper was to assess the runaway reaction caused by the operator error and design suitable reactor protection systems. The problems that could be foreseen immediately were:

- the high explosion pressure rules out total containment;
- a very large vent is likely to be used; and
- the high toxicity of the chemicals suggests venting is not an ideal solution.

The process and the associated hazards were analysed in stages, starting with experimental work to

investigate the basic explosion hazard. The full range of tasks were the following, described in the course of this paper:

- preliminary closed cell thermal runaway tests to quantify the hazard;
- specific tests replicating plant operating conditions;
- development of vent-sizing philosophy;
- tests to obtain data for vent-sizing;
- tests to obtain disposal system design data.

Quantification of thermal explosion hazard

Experimental details

The basic reaction to be studied is that between the cyanide and formaldehyde, initiated by an amine, representing an operating error as previously discussed. The experimental work was performed in the PHI-TEC II calorimeter (see *Figure 1*)¹. This device consists of a sample container of approximately 120 cm³ capacity which is suspended in the centre of a set of metal plates. The plates totally surround the sample container and are electrically heated. When a test sample undergoes reaction leading to a rise in temperature, the heated plates are controlled to match this temperature, thus eliminating heat losses from the sample.

The sample container used in most experiments is 0.006 in. wall thickness, which results in a very low thermal mass in relation to the mass of the test sample. This aspect is normally expressed in terms of the ϕ -factor:

$$\phi = 1 + (MC_p)_t / (MC_p)_s$$

The value of ϕ in large-scale plant is close to 1.0; using thin-walled test cells, the calorimeter is able to achieve very similar values.

In order to prevent the thin test cell from rupturing

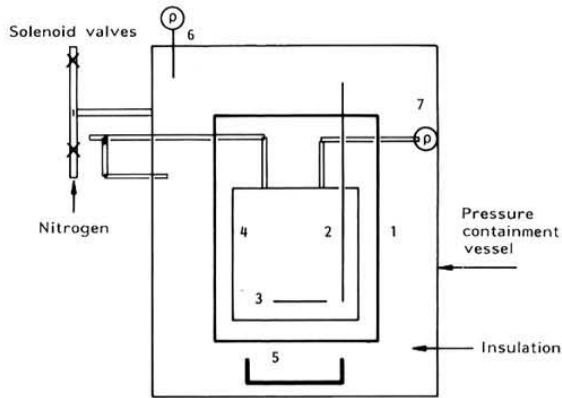


Figure 1 PHI-TEC Calorimeter for the assessment of reactive materials. 1, Three radiant heaters; 2, Sample thermocouple; 3, Magnetic bars; 4, Test cell; 5, U Magnet; 6, Vessel pressure transducer; 7, Sample pressure transducer

when the vapour pressure in the reacting sample rises, a nitrogen pressure is exerted outside the cell. Thus, as the reaction proceeds, pressure equalization is maintained by an electronic control system.

A consequence of these design features is that it is possible to test runaway reactions and apply the results directly to large-scale equipment. Extrapolation of test data is not required.

Preliminary test results

A number of tests were performed to provide an overall understanding of the hazard posed by the undesired reaction, looking at the effect of reactant concentration, initiator type and initiator quantity. A sample of these results is shown in *Figure 2* in the form of temperature against time.

The tests were performed by remote injection of the initiator into a cell containing the cyanide formaldehyde mixture at room temperature. In all cases, the reaction temperature is seen to rise immediately after the addition of an initiator, and then a variety of trends are observed depending on the test conditions. The main conclusions arising from these tests were:

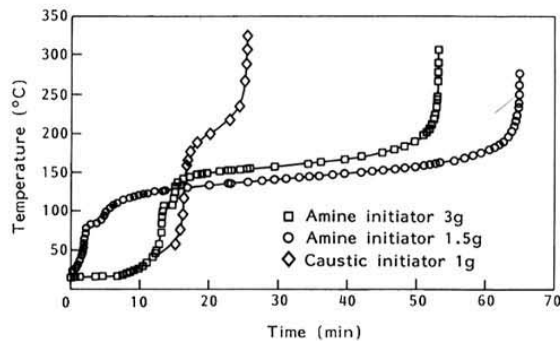


Figure 2 Cyanide thermal runaway

- dilution of the reactants has a significant effect on slowing down the rate (more than expected from simple quenching);
- initiator type (even though both initiators are alkaline) is important;
- quantity of initiator is very important.

It was clear that in order to proceed, these variables had to be defined more precisely and related back to the process. This was done and further tests with a specific initiator were completed; the results are shown in *Figure 3*. The two curves are for the same set of conditions except for the age of the cyanide sample (differing by about one week). The fresh sample gives the most rapid exotherm and this was used as the basis for the vent design. The pressure followed a similar trend to the temperature, rising rapidly at first then slowing down before accelerating again. The final pressure reached was about 110 bar – the pressure would have gone still higher if the test cell had not ruptured.

Venting strategy

The batch reactor being studied is operated at atmospheric pressure and therefore the normal approach is to set the relief device to open at about 1.5 bara, soon after the exotherm has been initiated. Looking at the manner in which the exotherm develops (see *Figure 3*, for example), the initial period is distinguished by an extremely rapid rise in pressure and temperature. The rate of change with temperature is shown in *Figure 4*. In order to cope with the initial rate, the relief device would have to be extremely large.

It was therefore decided that the vent should be set to cope with a later, slower rate of rise; *Figure 4* shows that at about 150°C, the rate slows down quite considerably and remains slow until about 200°C. The pressure corresponding to 150°C is about 5 bara, the vent was therefore sized for the self-heat rate at this point.

Although the vent is to be sized for a self-heat rate corresponding to 5 bara (150°C), it is of course still quite acceptable to set the vent opening pressure at the nominal 1.5 bara. Generally, the lower the vent opening pressure, the better. However, this was found to be

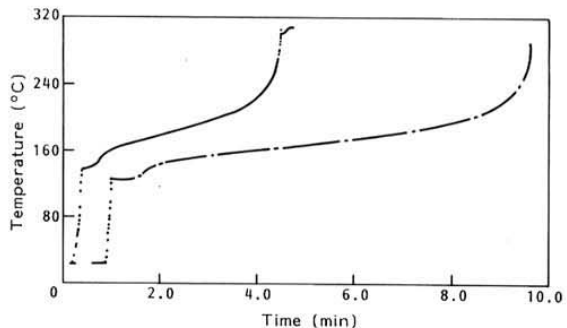


Figure 3 Runaway exotherm: effect of sample ageing (—: fresh sample; - - -: aged sample)

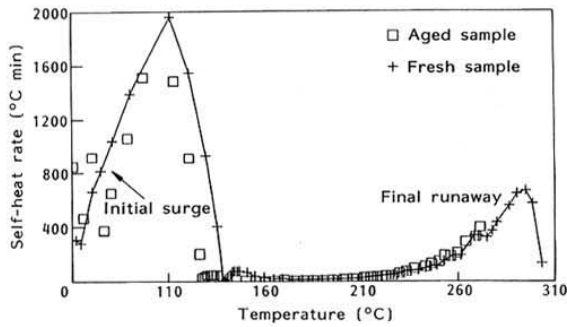


Figure 4 Variation in reaction rate during exotherm

an unacceptable philosophy in this particular case because of the toxic nature of the cyanide reactant. Analysis of the test data indicated that the cyanide is consumed in the first, rapid exotherm; therefore, if the vent is kept closed up to this point, the vented materials will have a substantially lower toxicity.

The venting strategy was therefore to size the bursting to accommodate the exotherm at 5 bara and 150°C and to set it to open at this pressure. The reactor was designed for about 8 bara and therefore this approach presented no problem.

Relief size evaluation

Information required

In order to size the vent consistent with the above strategy, it is necessary to determine the following:

1. The type of chemical reaction, in particular whether the reaction generates non-condensable gas (so-called gassy reaction), or whether it is 'vapour pressure' system where the reaction can be 'tempered' by latent heat cooling, or indeed some other combination.
2. The reaction rate parameters, depending on the type of reaction.
3. Physical property data.
4. Reactor configuration (volume, vent line length, reactor charge.)

Reaction type

The reaction was established as a vapour pressure type based on a number of items of information. The system pressure measured in the thermal runaway tests as a function reciprocal temperature, shown in Figure 5, provides the first clue as to the likely reaction type. Initially, the pressure is virtually independent of temperature (corresponding to the initial rapid exotherm) but then (during the venting period) logarithm of the pressure increases linearly with $1/T$. This behaviour is indicative of a pure vapour pressure system.

This observation was confirmed by further testing and the results are shown in Figure 6. In this test the exotherm was initiated in the manner described earlier

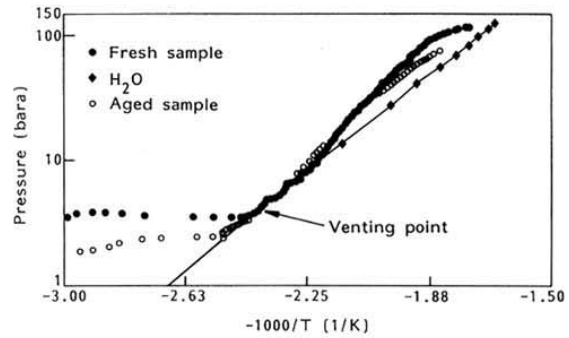


Figure 5 Pressure/temperature relationship

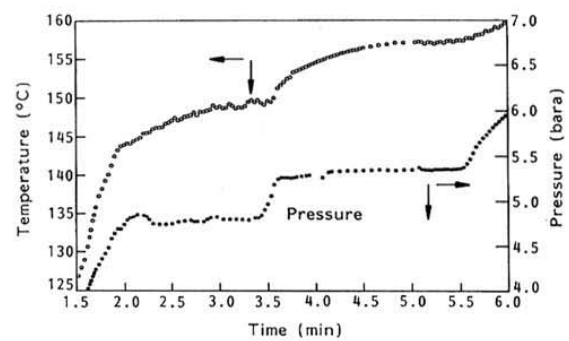


Figure 6 Tempered reaction verification

but then at the vent opening pressure (about 5 bara), the test cell was opened through a small opening and the pressure held constant. The test shows that when the pressure is held constant the temperature also turns around, the reaction being 'tempered' by the cooling due to latent heat of vaporization.

In Figure 7 this procedure was repeated at two pressures and the temperature clearly turns around in both cases.

Vent size calculation

Relevant equation. Since the reaction is a vapour pressure type capable of being tempered, then vent size

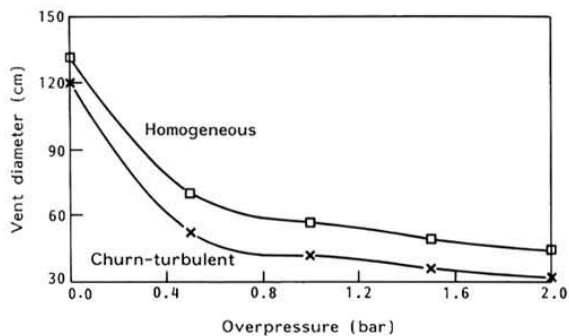


Figure 7 Vent diameter vs overpressure, 22 m³ reactor

may be calculated from Ref. 2:

$$A = \frac{M_o \bar{q}}{G \left[\left(\frac{V}{M_o} T_s \frac{dP}{dT} \right)^{1/2} + (C_p \Delta T)^{1/2} \right]^2} \quad (1)$$

where T_s is the temperature at the vent opening pressure (K), dP/dT is the slope of the pressure-temperature line for the reacting mixture (Pa/s), ΔT is the temperature rise corresponding to any overpressure above the vent opening pressure (K), \bar{q} is the average self-heat rate

$$\bar{q} = 0.5[(dT/dt)_s + (dT/dt)_m]C_p \quad (2)$$

where dT/dt is the rate of temperature rise, s at T_s and m at $T_s + \Delta T$, C_p is the liquid specific heat.

In the case of two-phase choked flashing flow (Ref. 2):

$$G \cong \frac{dP}{dT} (T_s/C_p)^{1/2} \quad (3)$$

Equation (1) is based on the assumption of homogeneous two-phase flow, that is, it makes no allowance for possible disengagement between vapour and liquid. The effect of disengagement will be considered later.

Derivation of data. The data required in Equation 1 can virtually all be obtained directly from the experiments already discussed. The pressure-temperature slope, dP/dT , may be measured from Figure 6 in the straight line part of the plot; this is equal to 1.0×10^4 Pa K⁻¹. The temperature at the venting pressure is confirmed by the 'tempering' test in Figure 6; this shows that $T_s \sim 154^\circ\text{C} = 427$ K. The rate of temperature rise, $(dT/dt)_s$ at the venting point is 70 K min^{-1} ($= 1.17 \text{ K s}^{-1}$); this is calculated from the temperature-time data at T_s .

The temperature rise corresponding to a given overpressure can be calculated directly from dP/dT :

$$\Delta T = \left(\frac{dP}{dT} \right)^{-1} \Delta P \quad (4)$$

where ΔP is the overpressure above the vent opening pressure of ~ 5 bara.

It is possible to calculate a range of ΔT and $(dT/dt)_m$ values corresponding to different overpressures; then, using Equation (1), the respective vent sizes can be determined. For an overpressure of 1 bar, for example, $\Delta T = 10$ K; the maximum temperature is therefore $T_s + \Delta T = 437$ K and $(dT/dt)_m$ at this temperature is 100 K min^{-1} .

Relief size for zero overpressure. Consider the vent size needed for the case of zero overpressure; i.e. $\Delta T = 0$ in Equation (1).

The self-heat rate \bar{q} at the vent opening pressure can be calculated thus:

$$\begin{aligned} \bar{q} &= 3200 \times 1.166 \\ &= 3730 \text{ W kg}^{-1} \end{aligned}$$

where $C_p \cong 3200 \text{ J kg}^{-1} \text{ K}^{-1}$ for the mixture. (Note that this is the only data used which was not directly measured in the test.)

The two-phase mass flux can be calculated thus:

$$\begin{aligned} G &= (10^4) \left(\frac{427}{3200} \right)^{1/2} \text{ kg m}^{-2} \text{ s}^{-1} \\ &= 3652 \text{ kg m}^{-2} \text{ s}^{-1} \end{aligned} \quad (5)$$

Taking a reactor of volume 22 m^3 and a charge of 10930 kg , substituting this data in Equation 1 gives:

$$\begin{aligned} A &= \frac{10930 \times 3730}{3652 \left[\left(\frac{22}{10930} \times 427 \times 10^4 \right)^{1/2} + 0 \right]^2} \\ &= 1.30 \text{ m}^{-2} \\ D &= 1.29 \text{ m}^{-2} \end{aligned} \quad (6)$$

This is the vent area for an ideal nozzle, without any allowance for overpressure above the set value.

Effect of overpressure and two-phase regime. Substantially smaller vent diameters are obtained if overpressure can be permitted. In terms of calculation, it is necessary simply to substitute in Equation 1 the value of ΔT corresponding to the overpressure desired. The rate of heat release would then be the average as given by Equation (2) instead of the value at T_s .

The results of such a calculation for the present system are shown in Figure 7; the vent diameter is reduced by more than a factor of 2 if an overpressure of 1 bar is allowed. Also shown in Figure 7 is the vent diameter if the churn-turbulent regime (Ref. 3) is assumed in place of homogeneous. This has the effect of reducing the vent size needed because it allows for some disengagement between vapour and liquid.

Effect of reactor charge. It is possible to alter the variables in Equation (1) and investigate the influence on vent size. An important consideration is the reactor charge; this is shown in Figure 8. The exercise is repeated for the churn-turbulent model. In both cases, substantial reductions in vent size may be obtained by reducing the initial charge.

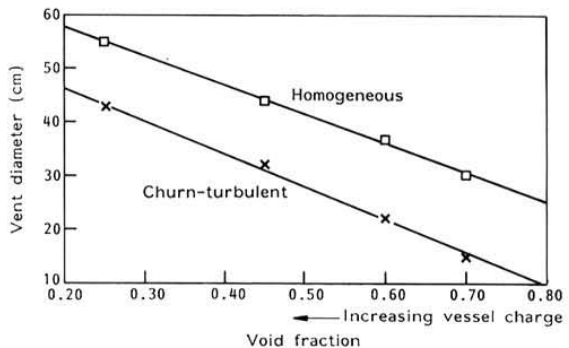


Figure 8 Vent diameter vs reactor charge, 22 m^3 reactor ($\Delta P = 2 \text{ bar}$, $\Delta T = 20^\circ\text{C}$, $H/D = 3$)

Nomenclature

A	Frictionless vent area (m^2)
C_p	Specific heat
G	Two-phase mass flux (kg/m^2)
M	Mass
M_o	Total (initial) mass of reactants (kg)
P	Pressure (Pa)
\dot{q}	Self-heat rate (W/kg)
s	Sample material
t	Test cell

T	Time (s)
V_o	Reactor volume

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