

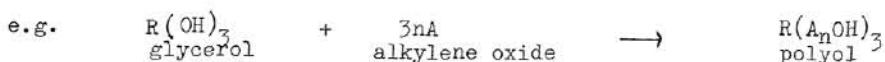
RELIEF OF RUNAWAY POLYMERISATIONS

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Liquid phase polymerisations such as Alkylene Oxide condensations are carried out in the presence of substantial proportions of a volatile reactant. This gives rise to the possibility of highly exothermic adiabatic runaway reactions. The reactor systems must ultimately be protected against overpressure by a relief device such as a relief valve or bursting disc. The quantity of reactants that could be released to atmosphere during the relieving of a runaway reaction depend on a complex inter-relation of temperature, pressure, reaction kinetics, vapour liquid equilibria and the characteristics of the relief device. A computer programme was developed to estimate this relationship and it was shown that relief valves rather than bursting discs minimise the loss to atmosphere.

INTRODUCTION

In the manufacture of polyols, polyhydric alcohols such as glycerol are condensed with ethylene and propylene oxide under pressure in large batch reactors,



Concentrations of up to 25% unreacted and volatile alkylene oxide in the polymerising reactant mass give rise, by equilibrium, to the reacting pressure of several atmospheres. As the reactions are catalysed and highly exothermic and the alkylene oxides are highly volatile and inflammable, robust mechanical design and generous heat transfer systems must be provided. Nevertheless, if things go wrong, adiabatic runaway reactions with fast temperature and pressure rises are possible, and have been observed.¹

Operator action, automatic control action, secondary cooling systems, emergency electricity generation and other automatic backup systems are extensively used but in the ultimate case if all these fail to operate the reaction system must still be protected mechanically by a relief device, such as a bursting disc or a relief valve which will exhaust the over-pressuring reactant gas to atmosphere.

The results of bursting discs rupturing have been observed on a number of smaller batch reactions under similar physical conditions, although of different chemistry. This led to concern about the understanding of sudden depressurisations of solutions of volatile organics from reacting masses. Massive entrainment was always deduced from the evidence; sometimes the whole parent batch was ejected. The area of contamination measured from the stack was often surprisingly large.

Bursting discs give a more "positive" guarantee of relief of a reactor. When they go they go. But the quantity of reactant released to atmosphere will be larger as there is no control of the release once the disc has ruptured. The subsequent risk of an unconfined vapour cloud ignition is therefore greater. This led to the re-examination of the discharge process during an adiabatic runaway reaction.

Relief Profile During an Adiabatic Runaway

The history of variables during the relief of a single volatile reactive component can be assessed using the following basic equations. As these are non-linear and interdependent they can be solved numerically on a computer. This has the advantage of making it relatively simple to carry out sensitivity analysis on the less certain data and assumptions. The equations define the mass and heat balances and the inter-relation between the phases.

Mass Balance

$$\text{Change in reactor mass} \quad \frac{dM}{dt} = F - V \quad \dots\dots\dots (1)$$

where F = feed rate and V is the venting rate.

(The feed is stopped automatically once the pressure has exceeded a preset value).

$$\text{Change in volatile reactant} \quad \frac{d(Mc)}{dt} = \frac{dM}{dt} - r$$

$$\text{but as} \quad \frac{dc}{dt} = \frac{1}{M} \frac{d(Mc)}{dt} - \frac{c}{M} \frac{dM}{dt}$$

$$\therefore \quad \frac{dc}{dt} = \frac{1}{M} (1 - c) \frac{dM}{dt} - \frac{r}{M} \quad \dots\dots\dots (2)$$

This assumes that only the volatile component is relieved.

Heat Balance

$$ms \frac{dT}{dt} = rH - VL \quad \dots\dots\dots (3)$$

This assumes adiabatic conditions. (This is approximately true for a fast runaway).

Kinetics

It has previously been shown (1) that the reaction rate is approximately first order with respect to oxide concentration.

$$r = kcS \quad \dots\dots\dots (4)$$

and the rate constant is described by the Arrhenius relationship

$$k = A \exp(-E/RT) \quad \dots\dots\dots (5)$$

By design the rate of reaction r_o is determined as a safe fraction Q_o of the normal available heat transfer capacity and

$$r_o = \frac{Q_o}{H} = c_o SA \exp(-E/RT_o) \quad \dots\dots\dots (6)$$

As c_o is known from vapour pressure data SA can be practically determined.

Vent Rate

The flow through the relief valve is sonic and is given by

$$V = K_p/T^{1/2} \quad \text{for } p > 1.1p_o \quad \dots\dots\dots (7)$$

The valve begins to open at p_o and is fully open at $1.1p_o$

When the valve is only partly open a correction has to be made giving

$$V = \frac{(p - p_o)}{0.1p_o} \cdot \frac{K_p}{T^{1/2}} \quad \dots\dots\dots (8)$$

This linear correction factor is a simplification.

Vapour/Liquid Equilibrium

This was measured in the laboratory at various reactant concentrations in the involatile polymer and gave an empirical correlation of the form

$$\ln p \approx Z_1 - Z_2/T \quad \dots\dots\dots (9)$$

where Z_1 and Z_2 are functions of c

Calculation Procedure

At the start of an adiabatic runaway the following are known:-

Reactor temperature	T_o
Reactor mass	M_o
Reactor heat removal rate	Q_o
Reactor pressure	p_o

From equation (9) C_o can be found by a simple iterative procedure.

The starting condition is now fully defined.

A small incremental time dt is selected so utilising initial values of $T, C, M,$

p and r are calculated from (9), (4) + (5), then dT, dc, dM from (3), (2), (1) and (7).

Revised values of T, c, M are thus found, and using a suitable iterative technique a solution is obtained.

Iterative technique

The first four points are set up using an Euler technique,

e.g. Firstly $T_1 = T_o + \frac{dT}{dt} dt$, hence find value of $\frac{dT}{dt}$ using first estimates of other variables.

Then New $T_1 = T_o + \frac{dt}{2} \left[\frac{dT}{dt}_o + \frac{dT}{dt}_1 \right]$

The calculation procedure can then be repeated until T_1 has converged.

A three term predictor/corrector method is then used. Euler is not used throughout because it is less accurate, and the errors are cumulative.

The next value of the variables estimated by the predictor,

e.g. $T_{n+1} = T_n + \frac{dt}{12} \left[23 \frac{dT}{dt}_n - 16 \frac{dT}{dt}_{n-1} + 5 \frac{dT}{dt}_{n-2} \right]$

The value of $\frac{dT}{dt}_{n+1}$ can be found using first estimates of the variables.

A better value is then derived by the corrector,

e.g. $T_{n+1} = T_n + \frac{dt}{12} \left[5 \frac{dT}{dt}_{n+1} + 8 \frac{dT}{dt}_n - \frac{dT}{dt}_{n-1} \right]$

This equation is used iteratively until it has converged.

The success of the technique can be tested in the programme by selecting different time steps (dt) and comparing solutions.

Major Assumptions

- a) Vapour - pressure data. Vapour pressure data for solutions of propylene oxide in polyol were obtained experimentally and correlated empirically. Generally, there is no need to go beyond the range of this data. However, the final temperature of an adiabatic runaway is in the range 200 - 300°C. The critical temperature for propylene oxide being 210°C. (though that of the binary mixture being considerably higher) deviations from the simple empirical relation at high temperature will occur. As the data had good fit and was measured to 220°C., extrapolation to 300°C. is justified.

The effect of the molecular weight of the polyol was found to be negligible for values above 2000. However this is not so for lower molecular weights. As there is inevitable scatter in experimental data, the correlation may also be used in the programme with ± 1 standard deviation.

- b) Reaction rate. The reaction rate equation was that given in reference 1. The temperature range over which this had been determined is limited - up to 140°C. It was assumed this could be reliably extrapolated using an Arrhenius type expression. The Arrhenius constant was chosen from similar published data, and varied in the programme to determine its effect.

It is implicit that the principal reaction scheme does not change. Side reactions at high temperature might form such products as allyl alcohol and propionaldehyde; it is assumed that the effect on pressure is small.

- c) Physical properties. For simplicity the following were assumed to be constant: specific heat of the liquid, latent heat of vapourisation, heat of reaction, activation energy.
- d) Vapour - liquid equilibrium. It is assumed that equilibrium conditions apply throughout an adiabatic runaway. Relief takes place over a finite time of several minutes, accompanied by bubbling in the reaction mass. It is considered justified that the system is therefore well mixed with little supersaturation. The presence of inerts in the reactor vapour space has been ignored. The effect will be to open the relief valve slightly earlier with respect to reaction temperature.
- e) Relief rate. The relief equation is based on sonic flow of vapour through an orifice. Two factors might limit this rate - two phase flow through the orifice, and back pressure in the relief duct. Fortunately it was possible to simulate reactor depressurisation under similar conditions to that of the relief valve lifting and this showed that the volume of liquid entrainment is very small. The relief duct is adequately sized. The inertia of the relief valve in lifting is not relevant as the time to open is relatively long.

Computed Results

The pressure and temperature history of a batch under runaway conditions obviously depends on the concentration and mass of unreacted volatile in the batch. This is highest at the end of addition of the major reactants and would give the greatest potential release. All simulated runaways were computed from this starting point. Typical pressure and temperature versus time curves are given in Figure I.

Four time zones are noted. In the first temperature and pressure rise until the preset relief valve pressure is reached. This takes about 4 minutes. In the second the relief valve opens from fully closed to fully open in about 2 minutes. In the third the relief valve is fully open. Pressure continues to rise for about 2 minutes, and finally as reactant is vented the relief valve will re-seat.

From rate of flow calculations through the relief valve the amount of organics sent to stack can be calculated. Sonic flow applies and rapid dilution with air by jet action entrainment disperses the gas. Nevertheless, large quantities (tons) of reactants can be released in this way but we have shown that the amount released through a relief valve is only a small proportion of that released when a bursting disc is ruptured at the same pressure. We are removing bursting discs and relying more and more on relief valves in this type of application on a judgement that the overall risk of a secondary atmospheric incident is reduced.

Some experiences with bursting discs

We have used bursting discs in about 50 instances and have recorded failures of many of them. Most have failed in unexpected ways and these have been investigated.

Maintenance records indicate the following abnormal causes as the most common:-

Corrosion - particularly of nickel discs due to atmospheric sulphides.

Atmospheric dirt working its way into the disc/holder niche due to disc flexing under repeated pressure reversal.

Wrong disc replacement by fitter. Said to be impossible by manufacturer.

Disc supplied of too thin material.

In most of the above cases failure of the disc was partial, often only a minute pinhole occurred. As these are sometimes difficult to detect and can lead to dangerous stack conditions, we often now use double discs with pressure indication or alarm between the discs.

With the few cases of disc failing as designed we noted massive entrainment of the parent batch, e.g. :-

A reactor containing about 70% non-volatile in 30% w/w methanol relieved at about 50 psig. More than $\frac{1}{3}$ of the non-volatiles were lost by entrainment over a period of about 10 minutes and an area approximately 50m radius.

A reactor containing about 70% polymer in 30% w/w freon relieved at about 70 psig. A third of the material was lost.

For the alkylene oxide polymerisation deliberate experiments were carried out depressurising the reaction mass into an evacuated space. While the reaction was observed to rise due to expansion of the mass, degassing was easy enough to limit the entrainment to that due to the finer droplets.

Another manufacturer has reported (private communication) that a batch of ethoxylate ejected totally through bursting disc failure. The sizing of relief areas for polymerisation is a subject of considerable interest and debate at the moment. Some guidance is given in References 2 - 4.

CONCLUSION

By analysing the heat and mass balance, kinetics, vapour liquid equilibria and relief valve characteristics for a batch polymerisation, it has been possible to create a computer programme which simulates the runaway conditions. This has given us greater confidence that relief valves will contain the runaway within safe boundaries, and may therefore be better than bursting discs by reducing the overall risk and minimising the loss of reactants to atmosphere. The programme also enables the testing of the more sensitive assumptions.

NOMENCLATURE

- A = A constant
 c = concentration of volatile reactant Kg/kg
 E = activation energy Kcal/mole
 F = feed rate Kg/hr
 H = heat of reaction Kcal/Kg
 K = relief valve constant
 k = reaction rate constant (hr)⁻¹
 L = latent heat Kcal/Kg
 M = mass in reactor Kg
 P = absolute pressure - vapour pressure of reactant. Bars.
 p_s = relief valve set pressure bars.
 Q = heat removal rate Kcal/hr
 r = reaction rate Kg/hr
 R = gas constant
 s = specific heat Cal/°C.g
 S = catalyst charge Kg
 T = absolute temperature °K
 V = venting rate Kg/hr
 Z₁, Z₂ = constants

subscripts

- ₀ = condition at start of runaway

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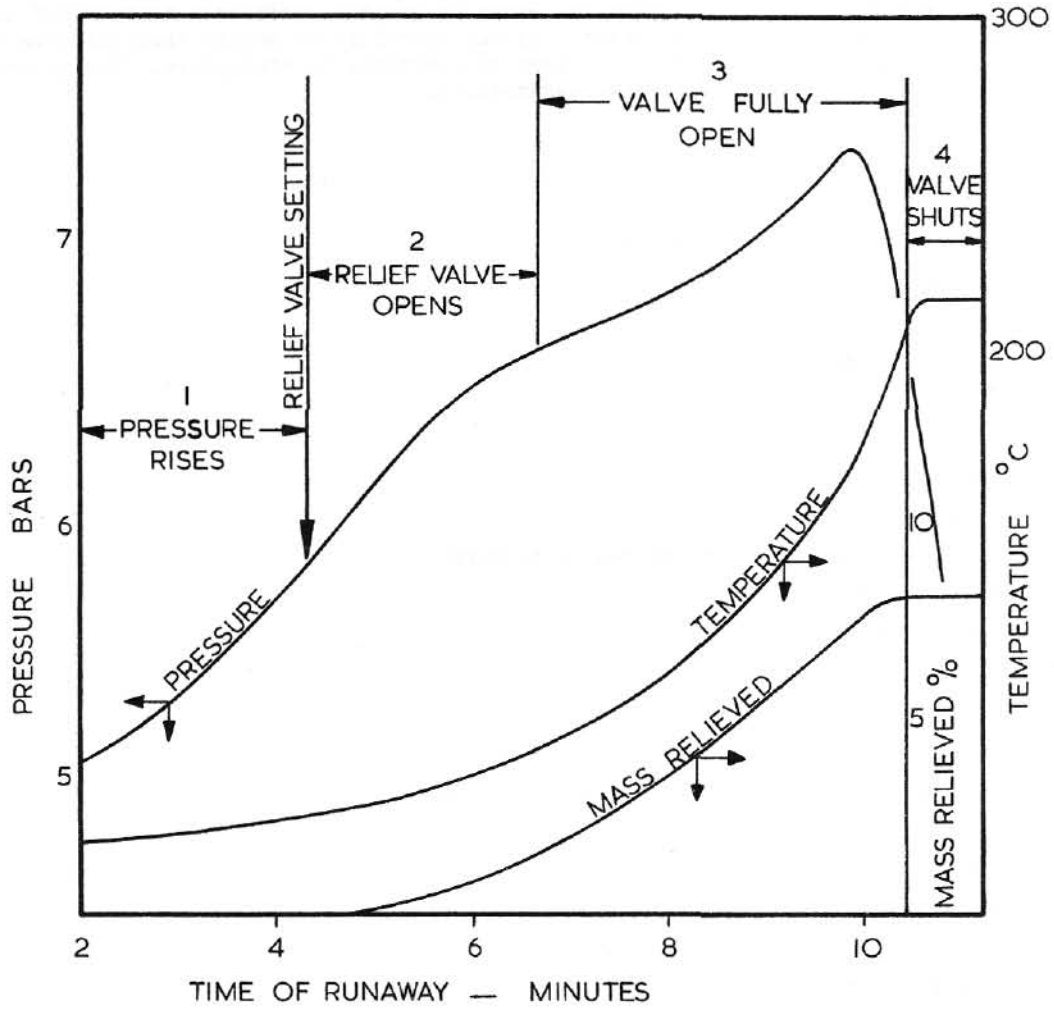


FIGURE 1. PRESSURE, TEMPERATURE AND MASS RELIEVED DURING ADIABATIC RUNAWAY WITH RELIEF.