LARGE-SCALE EVALUATION OF VENT-SIZING METHODOLOGY FOR VAPOUR-PRESSURE SYSTEMS

T J Snee[1,2], J Bosch Pagans[1], L Cusco[1], F Gallice[1,3], C Hoff[1,3], D C Kerr[1], A Rovetta[1,3] and M Royle[1]
[1]Health and Safety Laboratory, Buxton, SK17 9JN, UK
[2]Corresponding author: timothy.snee@hsl.gov.uk
[3]Sanofi - Aventis

A large-scale facility for investigating the performance of emergency pressure relief and disposal systems for chemical reactors has been constructed at the Health and Safety Laboratory as part of the EU AWARD Project. The facility has been used to investigate venting of the runaway reaction between water and acetic anhydride. Results are reported for a series of experiments in the 2,500 litre reactor over a range of batch volumes, along with data obtained previously using a 350 litre vessel. In some of these experiments, a small quantity of surfactant was added to the reaction mixture in order to change the void fraction distribution and investigate how this affects the maximum pressure in the reactor. Temperature, pressure, differential pressure and void-fraction measurements are used to establish the mechanisms which determine the maximum pressure and temperature in the reactor during pressure relief. This analysis is compared with the assumptions made in the most widely used design calculation methods for vapour pressure systems. Differences between the experimental results and current assumptions are identified. The safety implications of these discrepancies are explored.

INTRODUCTION

A wide range of techniques are available for designing emergency vents for runaway reactions where the overpressure is due to elevated vapour pressure of reagents and products[1]. Many of the methods for vapour pressure systems were developed as part of the DIERS project[2]. Some companies rely on dynamic computer modelling to determine the size and operating conditions for the relief system but most vents are designed using simplified equations. Both approaches require chemical kinetic and physical property data for the reaction system and models to predict level swell in the reactor and the two-phase flow regimes in the reactor and vent line. The relationship between pressure, temperature and the rate of heat production for a reaction system can be determined reliably using adiabatic calorimetry. Prediction of the flow regimes and the onset of two-phase flow is more problematical. The simplified equations and the dynamic computer models both contain assumptions about level swell, the void fraction distribution in the reactor and the ratio of liquid to vapour entering the vent line. The validity of these assumptions determines whether the mechanism of pressure turnaround, implicit in a particular calculation

method, is correct. For example, whether pressure turnaround is due fundamentally to tempering, vessel emptying or reactant consumption. Limits of applicability are often specified in connection with a particular calculation method but these limits have no significance if the fundamental assumptions are not correct.

MECHANISM OF PRESSURE TURNAROUND

The simplest and most conservative approach to vent sizing is to design for no overpressure. If the rate of heat generation at vent opening is equal to the rate of heat removal due to vapour generation, the reaction will be fully tempered and the pressure and temperature will gradually decline. However, large vent areas are required in order to achieve pressure turnaround at vent opening, particularly if the required volumetric flow rate of vapour is subsequently reduced due to two-phase flow. Substantial reductions in the required vent area can be achieved, if the maximum pressure (P_{max}) can be allowed to exceed the relief set pressure. However, this may affect the mechanism of pressure turnaround, producing, for example, a transition from tempering to vessel emptying or reaction completion.

The mechanism of pressure turnaround, during venting with overpressure, can be distinguished by the following characteristic features:

Tempering
With a relatively high proportion of vapour in the discharge stream, the increase in pressure above the relief set pressure increases the mass discharge rate of vapour until the rate of heat removal becomes equal to the rate of heat generation. At this point the temperature and pressure reach their maximum values and then gradually decrease.

Emptying
Two-phase flow, with a high proportion of liquid, causes the mass in the reactor to decrease rapidly. The rate of temperature rise is not strongly affected until the point is reached where the vessel is virtually empty and the rate of heat removal per unit mass becomes significant. Under these conditions, the temperature and pressure reach maximum values and then decrease rapidly at the point when the entire contents of the reactor have been discharged.

Reactant consumption
The ratio of liquid to vapour in the two-phase discharge from the reactor is not sufficient to empty the vessel rapidly but the proportion of vapour is insufficient to cool the contents and prevent the reaction from accelerating rapidly to completion. The temperature increases at an accelerating rate with no significant reduction in the rate of temperature rise at vent opening. The temperature and pressure go through defined maxima as the reaction nears completion. Two-phase flow continues after P_{max} and the reaction products cool due to vapour production. The final mass in the reactor is determined by the disengagement void fraction for the chemically inert system undergoing depressurisation.

The likely mechanism of pressure turnaround can be established by examining the relationship between pressure, temperature and reaction mass during a vented runaway reaction. In the present investigation, the characteristics of each mechanism of pressure turnaround are compared with the results of pilot and large-scale runaway reaction experiments performed at the Health and Safety Laboratory.

SIMPLIFIED EQUATIONS

The simplified vent sizing equations recommended by DIERS rely mainly on tempering and the emptying time principle. The most widely used equation was proposed by Leung [3]:

$$A = \frac{m_o \cdot q}{G \cdot \left[\left(\frac{V \cdot h_{fg}}{m_o \cdot v_{fg}} \right)^{1/2} + (C_f \cdot \Delta T)^{1/2} \right]^2} \tag{1}$$

where: A = vent area, m_o = initial reaction mass, q = heat production rate (averaged between the relief set pressure (P_{set}) and the allowable overpressure), G = mass flux, V = reactor volume, h_{fg} = latent heat, v_{fg} = difference in specific volume between vapour and liquid, C_f = liquid specific heat capacity and ΔT is the temperature rise between P_{set} and the allowable overpressure.

The rate of heat production in Equation 1 is assumed to have a constant (average value) between P_{set} and the allowable overpressure and the void fraction distribution in the reactor is assumed to be homogeneous. The homogeneous vessel assumption is also used in the calculation of G.

Equation 1 can be rearranged to give the emptying time directly:

$$t_{\text{emptying}} = \frac{m_o}{G \cdot A} = \frac{\left(\left(\frac{V \cdot h_{fg}}{m_o \cdot v_{fg}} \right)^{1/2} + (C_f \cdot \Delta T)^{1/2} \right)^2}{q} \tag{2}$$

If the runaway reaction is not mitigated by the cooling effect of vapour production, the available emptying time ($C_f \cdot \Delta T/q$) is obtained by setting h_{fg} to zero in Equation 2. This corresponds to the time, under adiabatic conditions, for the temperature to increase by ΔT above the temperature at P_{set}. The rate of temperature rise decreases and the available emptying time increases when some of the reaction energy is used to produce vapour. Under the homogeneous vessel assumption, the increase in available emptying time due to tempering, represented by $(V \cdot h_{fg}/m_o \cdot v_{fg})/q$ in Equation 2, is relatively small. As the allowable overpressure is increased, the emptying time is governed by increases in $C_f \cdot \Delta T$ while $V \cdot h_{fg}/m_o \cdot v_{fg}$ remains small and independent of overpressure.

In practice, there will be some degree of vapour-liquid disengagement and the emptying time will increase as the proportion of liquid in the discharge stream decreases. Increased disengagement increases the cooling effect due to vapour production and this may lead to tempering before the reactor is empty.

Because of disengagement, the homogeneous assumption leads to an overestimate of the mass discharge rate and, if pressure turnaround were due primarily to emptying, the maximum reactor pressure could exceed the calculated value. If the reaction is tempered, the homogeneous vessel assumption gives an underestimate of the cooling effect and the maximum pressure is likely to be less than the calculated value. If pressure turnaround is due to reactant consumption, the homogeneous assumption does not guarantee a conservative prediction of the maximum pressure.

PILOT-SCALE EXPERIMENTS

Maximum reactor pressures calculated using Equation 1 have been compared with the results of a large number of venting experiments using the 350 litre pilot-scale facility at the Health and Safety Laboratory. Various reaction systems have been investigated with a range vent areas, batch volumes and relief set pressures. In general, Equation 1 was conservative, yielding a calculated maximum pressure which exceeded the experimentally observed value. However, the degree to which the calculations were conservative depended on experimental conditions. There was no strong correlation between the calculated values and the observed variation in the maximum pressure. When the hydrolysis of acetic anhydride was investigated, in some cases, the experimental maximum pressures exceeded the calculated values. The cases included experiments in which surfactant was added to the reaction mixture. The variability in the degree to which some calculations were conservative and the non-conservative values for the hydrolysis reaction may arise because the pressure turnaround was not due to vessel emptying.

The experiments using the 350 litre facility were designed to establish directly whether a particular sizing method was conservative under the selected experimental conditions. However, where possible, additional instrumentation was provided to assess separate elements of the vent-sizing method such as the estimation of two-phase flow capacity, interpretation of the calorimetric data and level swell calculations to predict the onset of two-phase flow. The mechanism of pressure turnaround can be established from measurements of the mass of the reactor contents, the mass discharge rate and the void fraction at vent-line input. These data are difficult to obtain during rapid discharge from a relatively small glass-lined reactor. However, with detailed interpretation of the response from a gamma-ray densitometer mounted on the vent line and indications from load cells mounted under the catch tank, the results suggested that, in most cases, pressure turnaround was not primarily due to mass depletion.

Observed temperature and pressure variations at vent opening for a series of pilot-scale experiments can also be used to distinguish between possible mechanisms of pressure turnaround. A progressive reduction in vent area or an increase in batch volume is expected to produce a transition from full tempering to conditions under

which turnaround is either due to emptying or reactant consumption. A transition to vessel emptying would give a gradual increase in the maximum pressure, as conditions are made more severe. By contrast, because of the exponential dependence of reaction rate on temperature, a transition from tempering to rapid reactant consumption is evident when small reductions in vent area or small increases in batch volume produce an abrupt increase in the maximum temperature and pressure.

METHANOL-ACETIC ANHYDRIDE REACTION

Results from three pilot-scale experiments on venting of the reaction between methanol and acetic anhydride are summarised in Table 1. The batch volume and relief set pressure were held constant while the vent area was reduced progressively. The table shows no significant increase in P_{max} when the vent diameter was reduced from 35 to 25 mm but a further reduction to 15 mm caused an increase in P_{max} from 200 to 439 kPa. The mass remaining in the reactor increased when the vent diameter was reduced from 35 to 25 mm but the further reduction in vent diameter produced no substantial change in the final mass.

Figures 1 and 2 show the temperature and pressure records from the experiments with 25 and 17.5 mm vent diameters, respectively. Both figures show that, after vent opening, the temperature in the vapour space at the top of the reactor becomes equal to the liquid temperature, indicating the onset of two-phase flow. On vent opening, the temperature records in Figure 1 show a progressive reduction in the rate of rise until, after about 70 sec., a maximum is reached, indicating full tempering with equality between the rate of heat production and heat removal.

Figure 2 shows no significant reduction in the rate of temperature rise at vent opening. Pressure and temperature continue to increase rapidly, reaching a maximum after 240 sec. The temperature records show that the reduction in vent diameter has reduced the rate of cooling due to vapour removal but the increases in the mass discharge rate as the pressure rises has not been sufficient to empty the vessel before the reaction proceeds to completion. For the experiment with a 17.5 mm vent diameter, the total mass discharged was 38% of the initial mass. The proportion discharged up to P_{max} would have been substantially lower and the corresponding reduction in the total rate of

Table 1. Summary of results from pilot-scale experiments on reaction between methanol and acetic anhydride with batch volume of 250 litres and relief set pressure of 200 kPa

Vent diameter (mm)	Maximum pressure (kPa)	Maximum temperature (K)	Final reaction mass (kg)
35	200.2	360.8	109.6
25	200.8	364.2	145.1
17.5	436.8	394.7	147.5

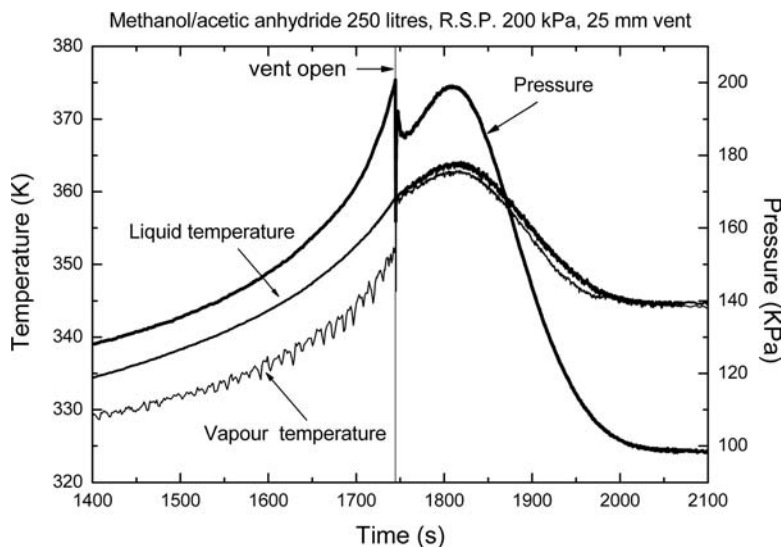Methanol/acetic anhydride 250 litres, R.S.P. 200 kPa, 25 mm vent

Figure 1. Temperature and pressure variations during pilot-scale venting of runaway reaction between methanol and acetic anhydride with a 25 mm vent diameter (batch volume 250 l: relief set pressure 200 kPa).

heat generation would have been small compared with the increase in rate due to the temperature rise between vent opening and the maximum temperature (T_{max}). With rapidly increasing temperature, equality between the rate of heat production and heat removal would have occurred only when the reaction neared completion.

HYDROLYSIS OF ACETIC ANHYDRIDE

Pilot-scale experiments on the reaction between water and acetic anhydride were performed over a range of relief set pressures with batch volumes from 75 to 200 litres. For some experiments a small quantity of surfactant was added in order to investigate how the maximum reactor pressure is influenced by level swell and the degree of vapour-liquid disengagement in the reactor.

The temperature and pressure records from two pilot scale experiments on venting of the runaway hydrolysis with and without surfactant are shown in Figure 3. At vent opening, with no surfactant, the reaction is fully tempered and the temperature and pressure begin to decline as the reaction proceeds to completion. Under the same conditions except for the addition of surfactant, the pressure increases rapidly after vent opening and reaches a value 80% above the relief set pressure.
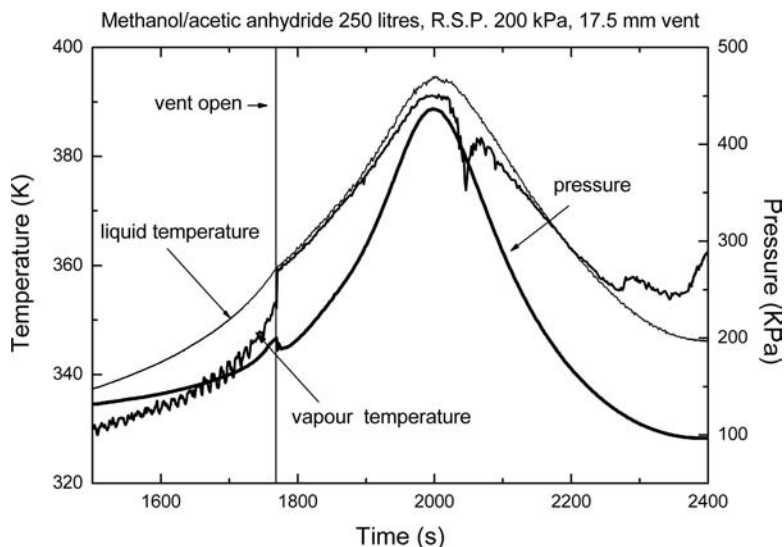
Methanol/acetic anhydride 250 litres, R.S.P. 200 kPa, 17.5 mm vent

Figure 2. Temperature and pressure variations during pilot-scale venting of runaway reaction between methanol and acetic anhydride with a 17.5 mm vent diameter (batch volume 250 l: relief set pressure 200 kPa).

Results of adiabatic calorimetry on the hydrolysis reaction with and without surfactant are shown in Figure 4. The addition of surfactant was found to have no effect on the adiabatic rates of temperature rise. Similarly, the presence of surfactant did not affect the pressure–temperature relationship. This means that calculations based on the closed system adiabatic data and the homogeneous vessel assumption give the same recommended vent diameter whether or not surfactant is present.

Maximum pressures calculated using Equation 1 were found to be less than the experimental values in five out of nine cases. With surfactant, the greatest difference was 1.0 bar and, with no surfactant and the highest batch volume, a difference of 1.2 bar was observed. However, the required vent diameters (without safety factors and calculated using a different procedure) were only slightly smaller than the actual diameter in three cases out of nine[5]. Detailed analysis indicated that the addition of surfactant or the increase in batch volume increased the proportion of liquid in the discharge stream and reduced the volumetric flow capacity for vapour. The corresponding reduction in heat removal due to vapour generation caused a transition from full tempering to conditions where the reaction proceeded rapidly to completion. Increased mass discharge rates and correspondingly reduced emptying times caused no significant reduction in maximum pressure. However, with relatively low batch volumes, integrated heat losses
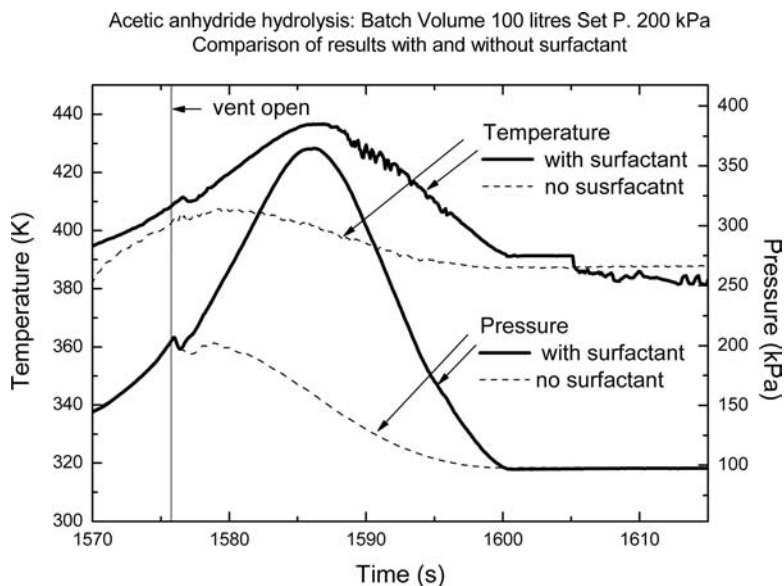
Figure 3. Temperature and pressure variations during pilot-scale venting of hydrolysis of acetic anhydride with and without surfactant (batch volume 100 l: relief set pressure 200 kPa)

due to vapour generation between P_{set} and P_{max} appeared to cause some reduction in the maximum pressure and temperature.

LARGE-SCALE EXPERIMENTS
The pilot-scale experiments on the hydrolysis of acetic anhydride have provided evidence for likely mechanisms of pressure turnaround and demonstrated that the maximum pressure cannot be predicted reliably unless the degree of vapour-liquid disengagement is known. Detailed analysis of the experimental data was required in order to establish the relative importance of tempering, emptying and reactant consumption and it was not clear how far conclusions from pilot scale experiments could be extrapolated to larger, industrial-scale, vessels.

LARGE-SCALE FACILITY
As part of the EU funded AWARD project, a large-scale facility was constructed at the Health and Safety Laboratory in order to investigate the reliability of emergency relief system (ERS) design methodology using a reactor similar in size to industrial vessels.
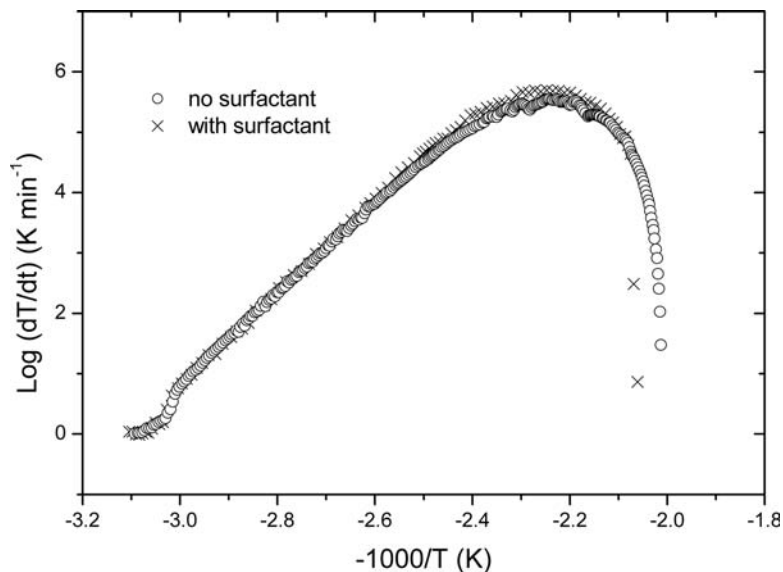
Figure 4. Adiabatic self-heat rate data for the hydrolysis of acetic anhydride

The facility, shown in Figure 5, comprises a 2,500 litre reactor connected via a 200 mm diameter vent line to a 13,000 litre catch tank. The height of the reactor is 3 m and was chosen to give a hydrostatic head similar to many industrial vessels. A diameter of 1 m was selected in order to facilitate the installation of specialised instrumentation to

Figure 5. Large-scale facility for investigating runaway reactions

determine the axial variation in void fraction in the reactor during venting and to limit the total volume so that the experiments could be performed safely. The contents of the reactor are heated and mixed by pumped circulation through an external heat exchanger. A large number of temperature and pressure transducers are installed at various points in the reactor, vent line and catch tank. Level swell and the density distribution in the reactor are determined using differential pressure and a specially designed scanning gamma-ray system.

The configuration of the gamma system is shown in Figure 6. Collimated gamma-ray beams emerge from source holders on one side of the reactor and rod-shaped detectors on the other side are used to monitor changes in attenuation caused by variations in the two-phase density in the vessel during pressure relief. Two systems have been installed to monitor density variations in the upper and lower halves of vessel. The sources are rotated in order to record the variation in attenuation as the angle of the beam changes. Under these conditions, the response from the detectors can be related to the axial variation of void fraction in the vessel.

The differential pressure sensors comprise a differential pressure cell connected by oil-filled lines to diaphragms which are bolted to the side of the reactor. The configuration of the sensors is shown in Figure 7. One of the transducers (DP101) records the pressure difference between diaphragms at the top and bottom of the reactor. The response is directly proportional to the mass of the contents and is not affected by the density distribution or absolute pressure in the reactor. The average density in the central section of the reactor can be calculated from the response of DP102. Bubbling in the bottom of the vessel and level swell above the upper diaphragm causes mass transfer in and out of the central
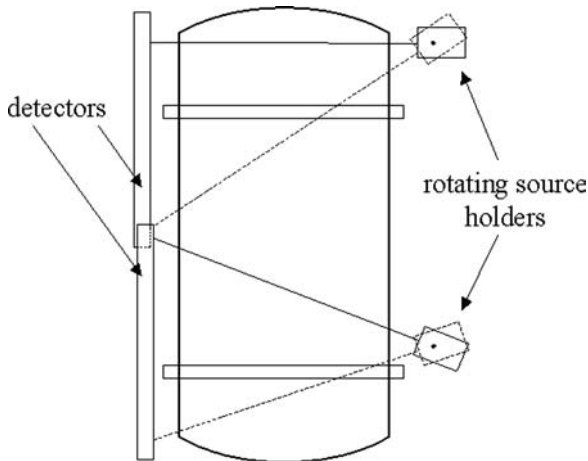

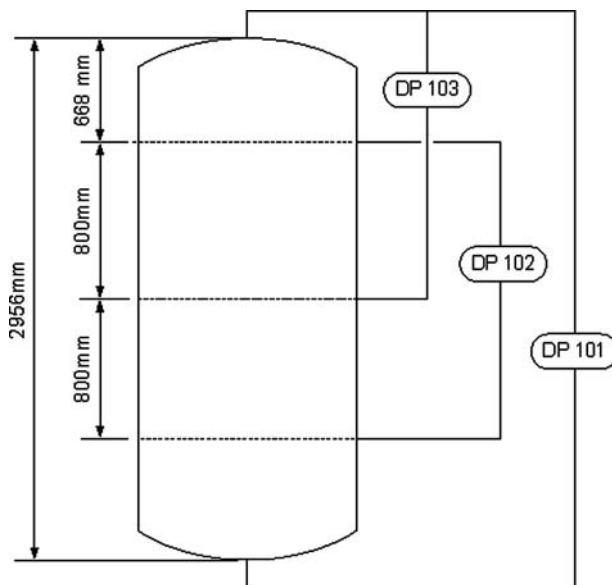**Figure 6.** Configuration of scanning gamma-ray system

Figure 7. Configuration of differential pressure sensors

zone. The net effect of the onset of two-phase flow can be to leave the average density unchanged. More gradual changes occur at the end of two-phase flow, which is indicated by an increase in differential pressure from DP102 as the level drops back toward the upper diaphragm followed by a decrease as bubbling subsides in the zone below the lower diaphragm. The third sensor (DP103) shows bubbling in the lower half of the vessel, causing level swell above the central diaphragm.

The runaway reactions were initiated by first heating acetic anhydride in the reactor to a temperature of 50°C and then charging an equimolar quantity of water. An actuated valve in the vent line was opened automatically at the relief set pressure (2 bara) to allow discharge from the reactor to the catch tank. A 100 mm diameter orifice plate was installed downstream from the actuated valve and the vent valve from the catch tank to atmosphere was kept closed during the tests.

RESULTS FOR HYDROLYSIS OF ACETIC ANHYDRIDE

The large-scale experiments were designed to determine the axial variation of void fraction in the reactor in order to assess the validity of various level swell models and assumptions regarding the flow regimes in the reactor and vent line. The analysis of these aspects has been reported elsewhere[4]. In the present discussion, the records of

11

Table 2. Summary of results of large-scale experiments on venting of the runaway hydrolysis of acetic anhydride with a relief set pressure of 2 bara

Initial fill	Maximum pressure (bara)	
	No surfactant	With surfactant
50 %	3.60	5.76
60 %	6.00	7.19
70 %	6.78	7.71

pressure, temperature and reaction mass and the evaluated void fraction distributions are used to determine the mechanism of pressure turnaround in the large-scale experiments. The enhanced instrumentation installed on the large-scale facility and increased reactor volume provide data on mass discharge rates and void fraction distributions which were not available from the pilot-scale tests and allow a more rigorous assessment of vent-sizing methodology.

Experiments, with and without surfactant, were performed over a range of batch volumes. The results are summarised in Table 2. The experiment with 50% fill and no surfactant gave a relatively small overpressure and Table 2 shows that the addition of surfactant or a small increase in batch volume produces a large increase in the maximum pressure. This parametric sensitivity was evident in the pilot-scale experiments and is likely to be associated with the exponential dependence of reaction rate and temperature. Further increases in batch volume produced relatively small increases in pressure.

Results from the experiments with an initial fill of 50% and no surfactant are shown in Figure 8. After vent opening at 2 bara, the pressure rises gradually and reaches a maximum at 3.60 bara and then remains approximately constant. At vent opening, the temperature in the vapour space at the top of the vessel increases rapidly to become equal to the liquid temperature at the bottom, indicating the onset of two-phase flow. At the same time, level swell to the top causes a sharp increase in attenuation of the beam scanning the upper part of the vessel. The end of two-phase flow is evident from the sharp reduction in attenuation approximately 25 sec after vent opening. The reduction in level causes an increase in the differential pressure in the central zone. The changes in attenuation beyond the period of two-phase flow are due to the gamma ray beam periodically passing across the flange in the upper part of the reactor. Mass discharge rates recorded by the top to bottom differential pressure sensor show a gradual decrease during the period of two-phase flow. The transition to vapour only flow results in slow changes in the reaction mass as the temperature and pressure remain approximately constant, indicating that equality between rates of heat generation and removal has tempered the reaction.

Figure 9 shows results from the experiment with surfactant and an initial fill of 50%. In contrast to the experiment without surfactant, the temperatures and pressure show accelerating rates of increase after vent opening and reach defined maxima after 19 sec.
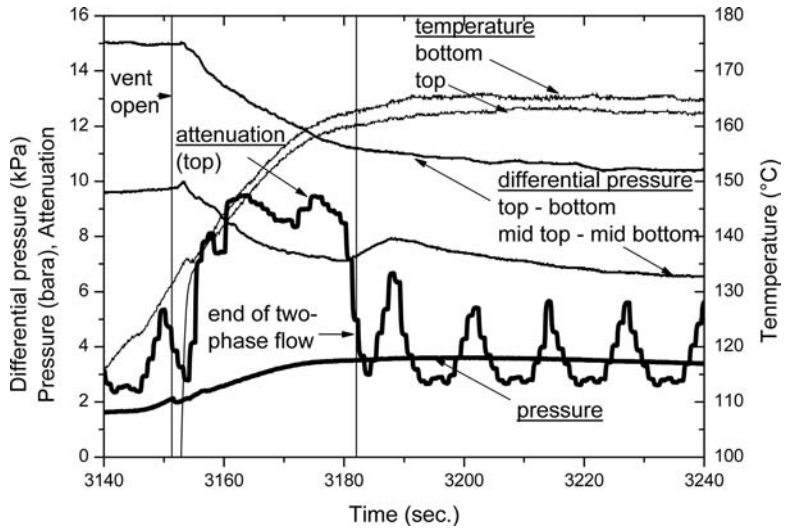
Figure 8. Variations in temperature, pressure and gamma-ray attenuation during large-scale venting of hydrolysis of acetic anhydride with 50% fill and no surfactant
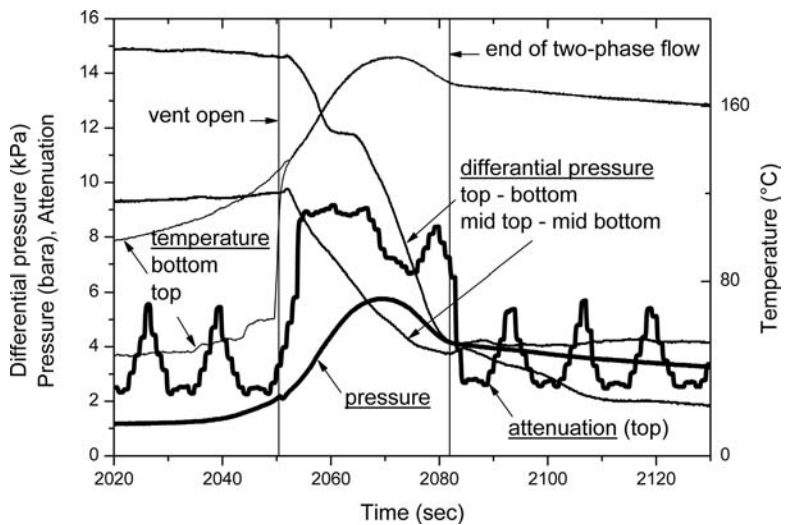

Figure 9. Variations in temperature, pressure and gamma-ray attenuation during large-scale venting of hydrolysis of acetic anhydride with surfactant and 50% fill

13

Two-phase flow is evident from the changes in vapour-space temperature, attenuation and the differential pressure in the central zone of the reactor. Two-phase flow continues beyond P_{max} and the mass discharge rates and total mass discharged are much higher than those observed without surfactant. The addition of surfactant is expected to increase level swell, producing a more rapid onset of two-phase flow and increasing the proportion of liquid entering the vent line. Comparison of Figures 8 and 9 shows that the increases in vapour-space temperature and attenuation are more rapid when surfactant is present. The attenuation, between vent opening at P_{max} is higher for the experiment with surfactant. Because of the exponential relationship between attenuation and density, this represents a large reduction in the void fraction at the top of the vessel. The increase in two-phase density in the vent line causes a marked reduction in the flow of vapour and the rate of heat removal from the reactor. With surfactant, the rates of heat removal are not sufficient to temper the reaction and the mechanism of pressure turnaround changes. The form of the pressure and temperature variations and, particularly, the records of reaction mass, strongly indicate the maximum pressure is determined by reaction completion rather than emptying.

The effect on the experimental results of increasing the batch volume from 50 to 60% is, in some ways, similar to the effect of adding surfactant. With a 60% initial fill (Figure 10), accelerating rates of pressure and temperature rise and increased mass discharge rates are accompanied by a large increase in the maximum pressure. The
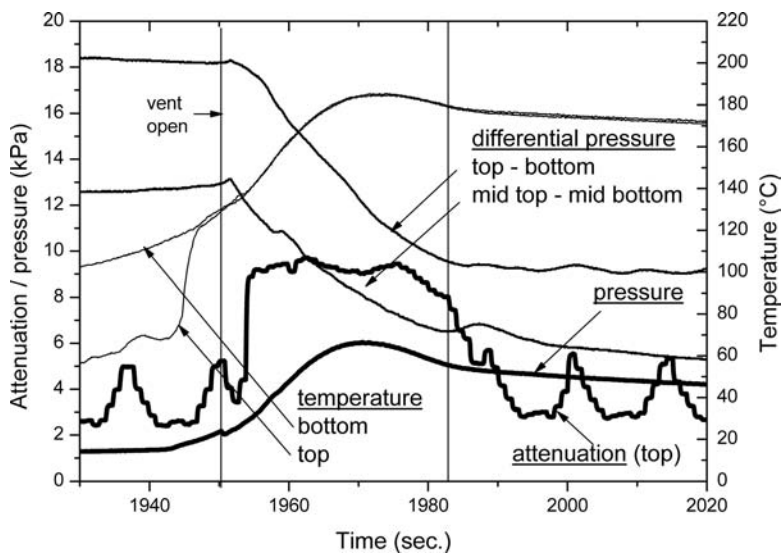

Figure 10. Variations in temperature, pressure and gamma-ray attenuation during large-scale venting of hydrolysis of acetic anhydride with 60% fill and no surfactant

Table 3. Relationship between mass discharge, rates of heat production and duration of two-phase for three of the large-scale venting experiments on venting of the hydrolysis of acetic anhydride

	between P_{set} and P_{max}				
	Mass discharged (%)	Increase in heat rate/kg (%)	Total mass discharged (%)	Duration of two phase flow (%)	Time from vent open to P_{max} (%)
50% fill no surfactant	27.0	129.7	30.2	26.2	42.2
50% fill with surfactant	29.6	161.7	72.1	29.4	19.0
60% fill no surfactant	33.2	162.0	49.0	32.6	21.3

vapour space temperature and attenuation variation, shown in Figure 10, indicate a more rapid onset of two-phase flow that observed due to the addition of surfactant (Figure 9). Earlier onset of two-phase flow will have increased the proportion of liquid entering the vent line and correspondingly reduced the rates of cooling due to vapour production. The results indicate that the increase in batch volume has caused a transition from tempering to a pressure turnaround caused by reactant consumption.

The preceding qualitative and semi-quantitative assessment of records from three of the large-scale experiments provides evidence for the mechanisms which determine the maximum temperature and pressure in the reactor. A quantitative indication of the relative importance of the underlying mechanisms is given in Table 3. The reduction in reaction mass at P_{max} is around 30% for each experiment and the total rate of heat production would be reduced proportionately. By contrast, the temperature increase between P_{set} and P_{max} produces increases in the rate of heat production of 130% for the tempered case and 160% for the other two experiments. This implies that, if gradual increases in the rate of vapour removal do not produce steady state tempering, equality between the rate of heat production and removal is unlikely to occur unless the reaction subsides due to reactant consumption. The untempered experiments (Figures 9 and 10) show sustained periods of two-phase flow and mass discharge after P_{max}, also implying that the pressure turnaround is not due to emptying.

VOID FRACTION DISTRIBUTIONS AND COOLING RATES
The changes in void fraction in the reactor during venting have been determined by combined interpretation of the data from the gamma system and the differential pressure cells[4].

In general, the addition of surfactant was found to reduce the void fraction entering the vent line, increase the void fraction in the lower part of the reactor and give an extended period of two-phase flow. Once the void fraction distribution has been established, vapour production and corresponding cooling rates can be calculated using the experimentally observed mass discharge rates and the void fraction at the top of the reactor. Results of these calculations for the experiments with and without surfactant and an initial fill of 50% are shown in Figure 11; along with heat production rates calculated using the adiabatic data. There are large fluctuations in the calculated cooling rates, particularly for the experiment without surfactant. Video records from a camera mounted on a sight glass at the top of the reactor indicate that the fluctuations are due to oscillations between two-phase and vapour-only flow before the complete transition to vapour only flow. With no surfactant, the increase in pressure after vent opening gives average cooling rates which are comparable with the rate of heat production. This causes a reduction in the rate of temperature rise leading to steady state tempered condition at 439 K, with equality between the rate of heat production and removal (Figure 11). With surfactant, the rate of cooling remains below the adiabatic rates of heat production and, as the temperature increases after vent opening, steady state conditions become impossible. Under these conditions, maximum temperature coincides approximately with the temperature at which the adiabatic heat production rate reaches a maximum. The final temperature increase is determined by the adiabatic temperature rise reduced by an amount related to the integrated
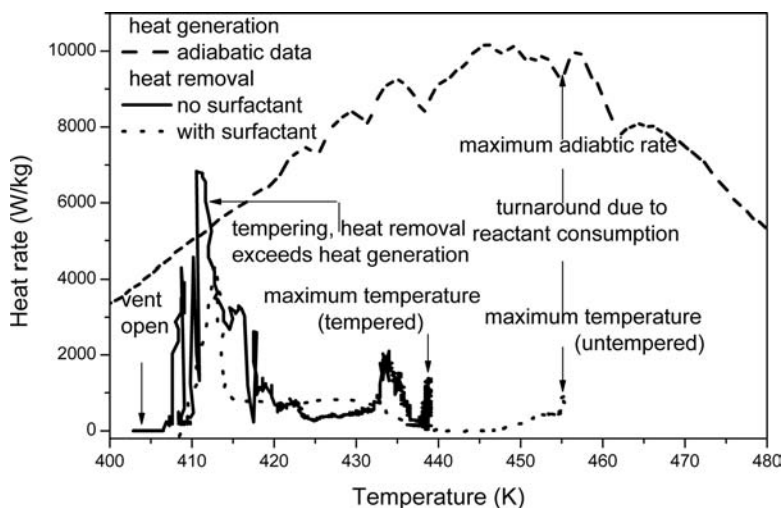

Figure 11. Adiabatic self-heat rate data compared with cooling rates calculated for large-scale experiments on venting of the hydrolysis of acetic anhydride with and without surfactant.

rates of heat removal due to heat transfer during the induction period and vapour generation after vent opening.

IMPLICATIONS OF ASSUMPTIONS ABOUT PRESSURE TURNAROUND

If the maximum temperature is determined by the total reaction enthalpy or adiabatic temperature rise, the maximum pressure may differ significantly from values calculated assuming tempering or vessel emptying at P_{max}. The simplified DIERS equations include self-heat rates averaged between P_{set} and P_{max}, without reference to the total exothermicity. If pressure turnaround is due to reactant consumption, the maximum pressure can be lower or higher than the calculated values, depending on the total heat of reaction. This can be seen from Figure 12, which shows adiabatic data for the hydrolysis reaction along with theoretical values for reactions with similar initial rates of heat production but differing heats of reaction. Each of these adiabatic data sets would give the same recommended vent area and, in principle, the reactions could be fully tempered at the same moderate overpressure. However, if the allowable overpressure was increased, relying increasingly on the emptying time principle, the corresponding reduction in vent
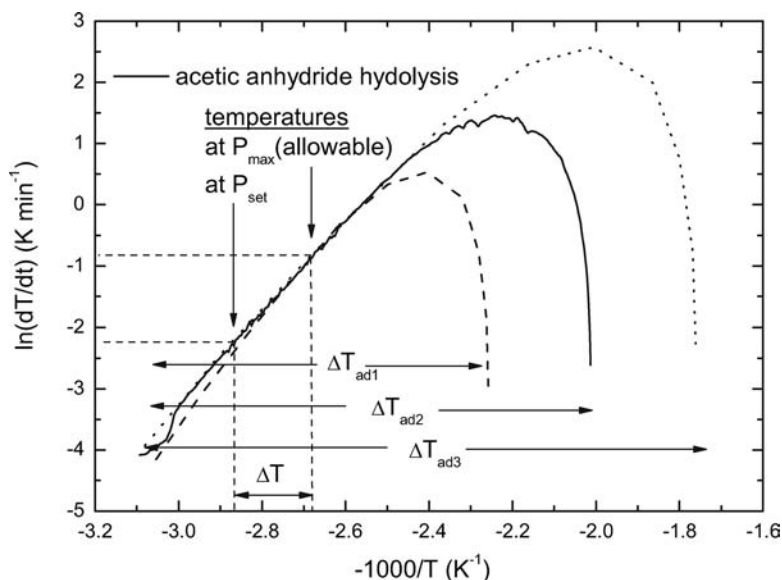

Figure 12. Adiabatic self-heat rate data for the hydrolysis of acetic anhydride compared with curves for theoretical reactions with similar initial heat rates but with heats of reaction and corresponding adiabatic temperature rises (ΔT_{ad}) which are above and below the value for the hydrolysis.

area could cause a transition from tempering to reaction completion at P_{max}. The maximum pressures for the theoretical reaction with the highest adiabatic temperature rise would be higher than those observed for the hydrolysis reaction. Alternatively, with a lower adiabatic temperature rise, the vent area could be lower than that obtained using the emptying time principle.

VENT-SIZING FOR REACTION COMPLETION

If pressure turnaround occurs due to reactant consumption, the following expression can be used to relate the recommended vent area to the maximum allowable temperature and pressure[5].

$$A = \frac{m_o}{G t_{ad}} \left(1 - \frac{1}{\exp\left(\dfrac{C_f (T_o + \Delta T_{ad} - T_{max})}{h_{fg} x}\right)} \right) \tag{3}$$

where: t_{ad} = adiabatic time between P_{set} and maximum temperature rate, T_o = initial temperature, T_{max} = maximum allowable temperature, ΔT_{ad} = adiabatic temperature rise, x = vapour mass fraction at vent line input.

Equation 3 is obtained by relating the rate of cooling due to vapour generation to the average mass discharge rate and the rate of heat production and integrating over the period between vent opening and the maximum adiabatic rate of temperature rise. Equation 3 gives larger vent areas as the heat of reaction increases and gives conservative predictions for the maximum pressures in the pilot-scale experiments, when the experimentally determined value of the inlet quality is used in the calculations. In common with the DIERS simplified equations and dynamic computer models, accurate implementation of Equation 3 is dependent on a reliable model for the flow regime in the reactor. When the homogeneous vessel assumption, implicit in Equation 1, is used to calculate the inlet quality and flow capacity in Equation 3, conservative vent areas are obtained for all of the nine pilot-scale experiments on the hydrolysis of acetic anhydride.

FURTHER INVESTIGATION

Large-scale experiments have been performed with and without surfactant over a limited range of batch volumes keeping the relief set pressure and vent area constant. The vent area was chosen to give sustained periods of two-phase flow, in order that changes in the axial variation of void fraction could be measured during the venting period. In the pilot-scale experiments, relatively larger vent areas were chosen in order to give a direct assessment of the reliability of simplified vent-sizing equations. The large-scale experiments provided data on mass discharge rates and void fraction distributions, which were not available from the pilot-scale experiments. Further large-scale tests

using larger vent areas should be performed in order to develop criteria for predicting whether tempering will occur. With larger vent areas, it may be possible to investigate conditions where emptying produces pressure turnaround before the reaction proceeds to completion.

CONCLUSIONS

A large number of pilot-scale venting experiments have been performed using a range of reaction systems, vent areas, batch volumes and relief set pressure. In general, the DIERS simplified vent-sizing equations gave conservative predictions of the maximum pressure. However, for the reaction between acetic anhydride and water with and without surfactant, in some cases, the observed pressure exceeded the calculated value. The difference between experimental and calculated values depended on the detailed calculation method. Some procedures gave recommended vent areas (without the use of safety factors) which were smaller than the actual diameter in only a few cases and, in these cases, the difference in vent area was small.

Detailed analysis of the pilot-scale results for the range of reaction systems indicates that either tempering occurred shortly after vent opening or the reaction proceeded rapidly to completion. Pressure turnaround due to emptying of the reactor was not observed in the pilot-scale tests.

Large-scale experiments on the hydrolysis of acetic anhydride were performed with instrumentation specially designed to determine the reaction mass and the axial variation in void fraction in the reactor during venting. The addition of surfactant, or a small increase in batch volume, produced large increases in the maximum pressure. This effect has been related to changes in the void fraction distribution and the mass discharge rate. Cooling rates, calculated from the mass discharge rates and the void fraction distribution, have been compared with rates of heat production derived from adiabatic data. The comparison shows how changes in the degree of vapour liquid disengagement in the reactor produces a transition from full tempering to conditions where the reaction accelerates to completion.

If the reaction proceeds rapidly to completion, the final temperature and pressure are determined by the thermochemistry and not the kinetics. Under these conditions, vent-sizing equations that do not contain the heat of reaction or adiabatic temperature rise cannot reliably predict the maximum pressure and temperature. Vent sizing equations based on the emptying time principle have the potential to under predict the maximum pressure, if the heat of reaction is relatively large. However, in other cases, with low heats of reaction, the vent areas calculated to empty the vessel rapidly could be adequate to protect the vessel. The pilot and large-scale results indicate that vent-sizing calculations, using current methodology, should include safety factors[6], unless the mechanism of pressure turnaround can be predicted with confidence. Further work is needed in order to establish whether the maximum pressure is generally determined by emptying, reactant consumption or tempering.

DISCLAIMER
The opinions expressed in this paper are those of the authors and do not necessarily represent those of the sponsoring organizations.

REFERENCES
1. Etchells, J C and Wilday, A J (1998), "Workbook for chemical reactor relief system sizing", http://www.hse.gov.uk/research/crr_htm/1998/crr98136.htm, HSE Contract Research Report 136/1998, HSE Books.
2. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", DIERS/AIChE, 1992, ISBN 0-8169-0568-1.
3. J C Leung, "Simplified Vent Sizing Equations for Emergency Relief Requirements in Reactors and Storage Vessels", AIChE Journal, 32, (10), 1622-1634, 1986.
4. Snee T J, Bosch J, Cusco L, Hare J A, Royle M and Wilday A J, 2005, DISPOSE: "Large scale experiments for void fraction measurement during venting," HSL Internal Report PS/05/03.
5. Snee, T J, Butler, C, Hare, J A, Kerr, D C, Royle, M and Wilday, A J, (1999), "Venting studies of the hydrolysis of acetic anhydride with and without surfactant (Vapour System 3)", HSL Report No PS/99/13.
6. Hare, J A, Wilday, A J and Owens, A, (2005), "Simplified methods for vent disposal system sizing for runaway chemical reactors: EC AWARD project guidance for SMEs", IChemE Hazards XIX International Symposium, Manchester, March 2006.