

Pilot Scale Reactor Venting Experiments for Gassy Systems and the Implications for Vent Sizing

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The Science and Research Centre of the Health and Safety Executive (HSE) performed two series of vented peroxyester decompositions at pilot scale in order to examine various gassy system vent sizing calculation methods. The first series of experiments explored the effects of batch volume and the second series the effects of vent line diameter on the reactor venting. This was to validate the DIERS vent sizing methods for gassy systems, to consider possible oversizing of vents when using these methods and to evaluate the vent sizing methods for gassy systems which consider transient mass loss. This paper presents the experimental and numerically calculated results from both series. The selected vent sizing methods which account for transient mass loss were applied and are described in this paper. A more simplified vent sizing method that does not account for back pressure and friction was also examined. Issues such as level swell, void fraction, maximum pressure and remaining reactor mass are explored. This paper also discusses the differences between the experimental and numerically calculated results. Overall, the DIERS sizing method is conservative when compared to experimental results whereas methods that account for mass loss due to venting were shown to be non-conservative at specific reactor fill levels. Options for further analysis are given.

Keywords: Reactor Venting, Gassy System, Vent sizing

Introduction

The Science and Research Centre of the HSE performed two series of vented peroxyester decompositions at a pilot scale. The first series explored the effects of batch volume and the second series the effects of vent line diameter on the reactor venting. Experimental results from both series are presented. An important purpose of the experiments was to explore various gassy system vent sizing calculation methods. Vent sizing methods which take account of transient mass loss and a simplified vent sizing method which does not account for back pressure and friction are described. Issues such as level swell, void fraction, maximum pressure and the mass left in the reactor are explored. Differences between the experimental and calculated results are discussed. The DIERS sizing method for gassy systems that takes no account of mass loss due to venting was conservative for the experiments. Methods that reduce the vent area by taking account of the mass loss due to venting were shown to be non-conservative at certain reactor fill levels. Options for further analysis are given.

Chemical Reactions are either exothermic, giving out heat or endothermic, taking heat from the surroundings. The rate of a chemical reaction increases as an exponential function of temperature. A runaway reaction occurs in a vessel when the rate of heat generation exceeds the rate of cooling. The basis of safety for the chemical reactor should normally prevent runaway and control the temperature so a runaway does not occur. Runaway reactions can be classified as vapour pressure, gassy and hybrid. The classification relates to the pressure generated as a result of the runaway reaction. In a vapour pressure system, the vapour pressure increases as the liquid temperature rises during the runaway. In a gassy system, the pressure increases due to permanent gas produced by the reaction. In a hybrid system, the pressure is due to both vapour pressure and permanent gas.

As a last line of defence reactor venting is used to control the temperature and prevent the pressure from bursting the vessel. When a bursting disc opens or a pressure relief valve operates, the vapour pressure and gassy systems behave in different ways. For a vapour pressure system, the heat required to generate the vapour causes the temperature to stop rising i.e. a tempered system. For a gassy system, no latent heat is required to generate the permanent gas and the temperature continues rising, i.e. an un-tempered system. Two-phase flow often occurs with the venting of runaway reactions. This is because the liquid in the reactor can be significantly swelled, by the rapid production of bubbles of gas or vapour, so that the liquid level reaches the vent. The two-phase flow regime can be either homogeneous (where the liquid and gas / vapour are uniformly mixed) or churn turbulent (where there are large bubbles in the liquid). Gas-only flow (or vapour-only flow) occurs when the liquid level does not reach the vent.

Figure 1 shows the typical behaviour of a gassy runaway reaction system during reactor venting (Etchells and Wilday, 1998). The bursting disc ruptures at its set pressure and some liquid may be vented for a short period. Thereafter, the pressure returns to atmospheric and remains constant as the temperature still continues to rise. Gas-only relief occurs during this period. At a much higher reaction rate, two phase relief begins and the pressure rises rapidly. This is due to the amount of gas generated in the swelling liquid which now reaches the reactor vent. If two phase flow occurs during venting then a larger vent size is normally required.

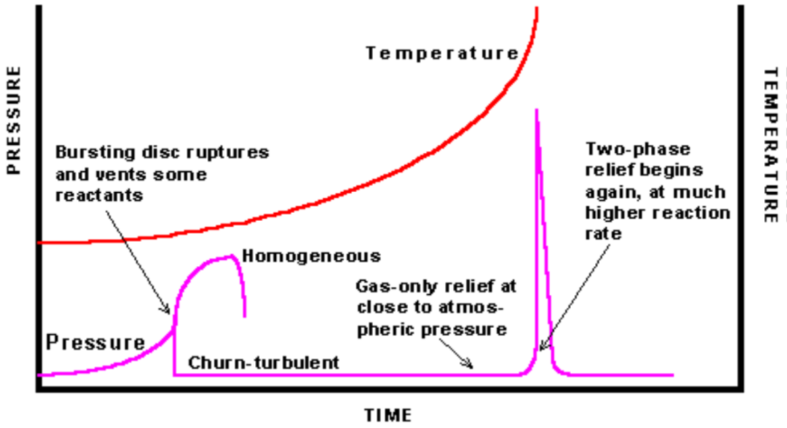

Figure 1 Typical Behaviour of a Gassy System (Etchells and Wilday, 1998)

The Experiments

The Science and Research Centre of the HSE performed pilot scale experimental work at Buxton on runaway reactions, supported by small scale experiments and vent sizing, to help validated the Design Institute for Emergency Relief Systems (DIERS) vent sizing methods. The DIERS methods for gassy system in particular have received only limited validation. The work is described in more detail in Etchells, Snee and Wilday (1998). Figure 2 is a schematic diagram of the pilot scale facility showing the reactor, vent line and catch tank, and associated instrumentation. There are thermocouples (TC) and pressure transducers (P) at various positions in the reactor, vent line and catch tank. The facility has various manual valves (MV) and automatic valves (AV) to allow material flows. Automatic valve AV32 behaves like a bursting disc because it opens at a predetermined set pressure and thereafter remains open. For the gassy system pilot reactor experiments, described in Etchells, Snee and Wilday (1998), the set pressure was always 2 bara and the reactor jacket was heated. Mass flow measurements included a densitometer, load cells on the vent line elbow and load cells under the catch tank.

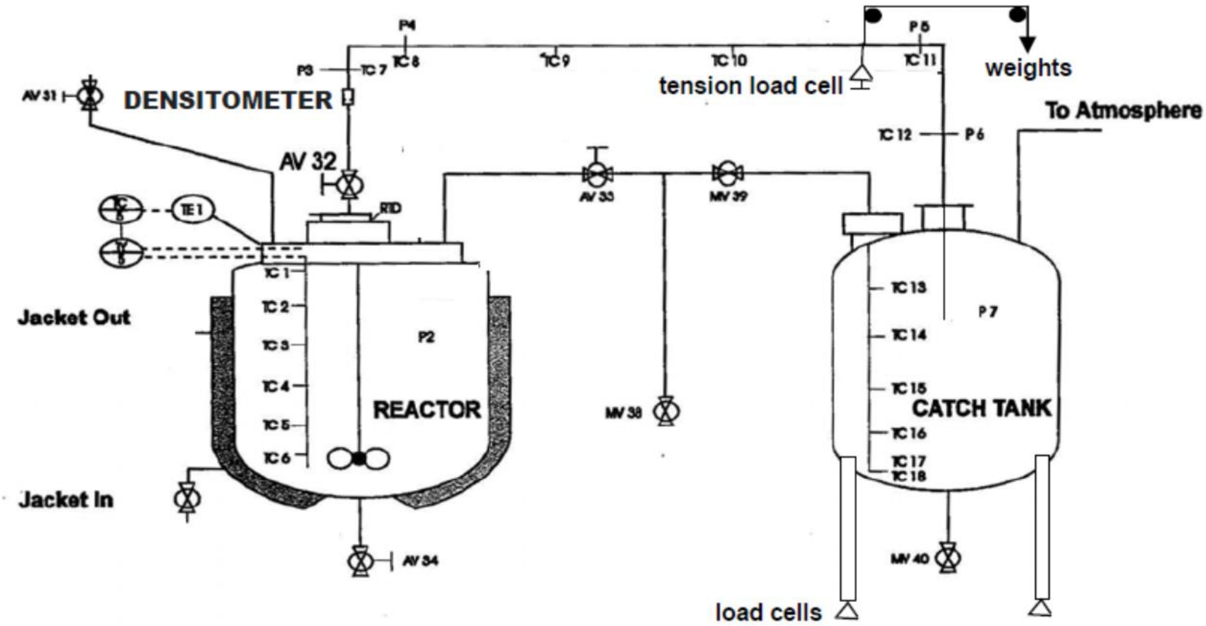

Figure 2 Pilot Plant Instrumentation

A peroxyester (Trigonox 21) was used in the experiments because it decomposes to give carbon dioxide, so giving a gassy system. The peroxyester has to be kept cool or diluted in a solvent to prevent decomposition. Dissolving Triogonx 21 in a solvent (Shellsol T) raises the decomposition temperature, making the pilot scale experiments safer; as the rector jacket has to be heated to give appreciable decomposition. A catalyst (NL49P) was used to increase the rate of reaction, so the decomposition occurred over a reasonable time period. Figure 3 shows how Trigonox 21 (tert-butyl peroxy 2-ethylhexanoate) decomposes to give carbon dioxide, various alkenes and tert-butanol. During the experiments, Triogonx 21 was dissolved in Shellsol T (an isododecane solvent) at 20 % by weight. The catalyst was the accelerator NL49P (with active ingredient cobalt octoate) at 1% by weight.

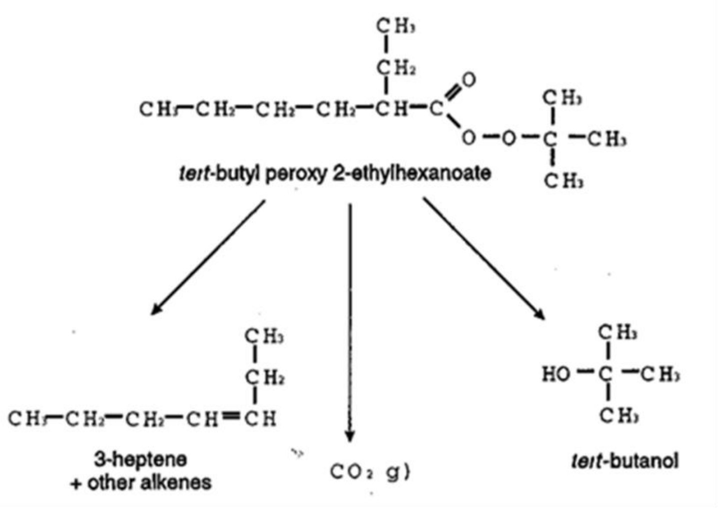

Figure 3 Decomposition of Trigonox 21

In order to derive vent sizing data, the decomposition reaction was also studied using a small scale adiabatic calorimeter (Phi Tec), based on the DIERS Vent Sizing Package (VSP) (Etchells and Wilday 1998). For gassy systems, open system tests are often preferred, as the maximum pressure will be lower and the effects of dissolved gas will be reduced, compared to closed system tests. In an open system test, the test cell is connected to the outer containment vessel of the Phi-Tec. Performing the open system test at the same pressure as the maximum pressure in the pilot reactor should give the most accurate venting results, as the large scale test will be experimentally simulated on the small scale. Thus open system tests were performed at various back pressures, corresponding to the maximum pressures obtained in the pilot-scale experiments with varied fill levels, see Table 3. Pressure and temperature data with time are needed to size the vent for a gassy reaction, using the conditions at the maximum pressure rate. Self-heat rate plots, showing the natural log of the temperature rate versus the reciprocal of temperature, indicate the heat of reaction and the reaction rate. Figure 4 is the self-heat rate plot of results for the perxoyester decomposition. Figure 5 shows pressure versus temperature. Figure 6 shows pressure rate versus temperature. The test with a back pressure of 2.73 bara was used for all the vent sizing calculations. The maximum pressure rate was 6.58 bar/min at a pressure of 3.16 bara and a temperature of 159.6°C; the temperature rate 298 °C/min

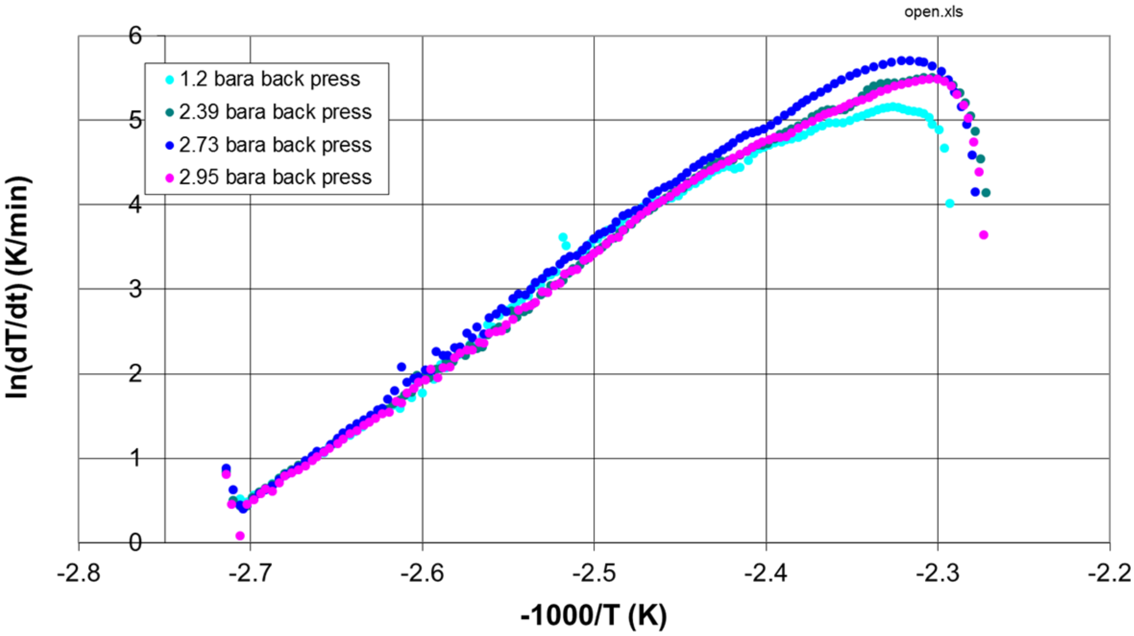

Figure 4 Open System Tests – Self Heat Rate

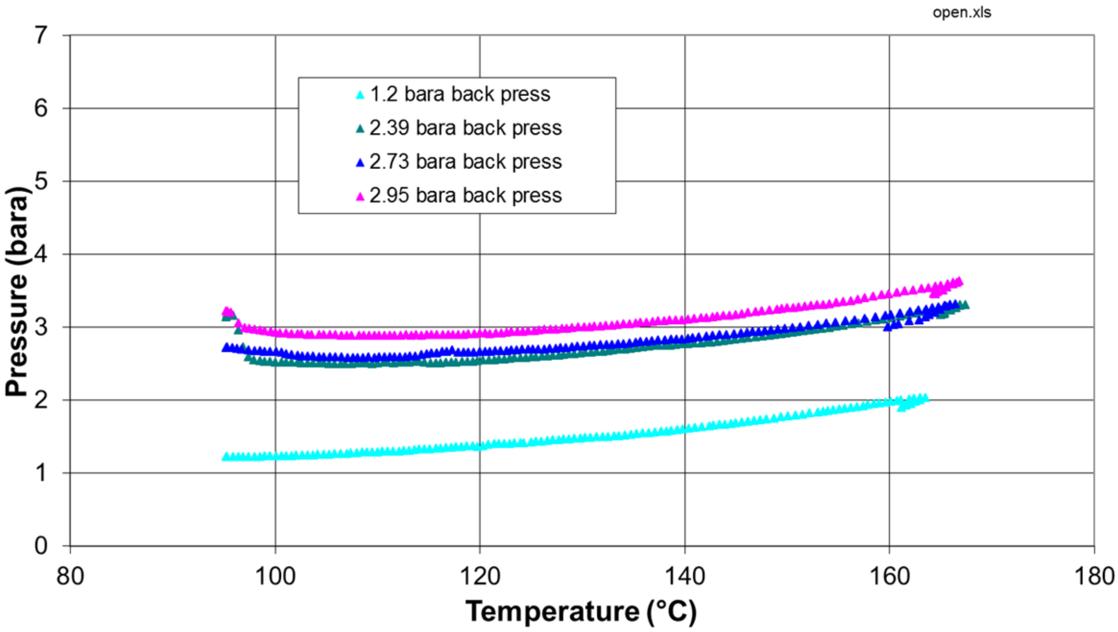

Figure 5 Open System Tests –Pressure versus Temperature

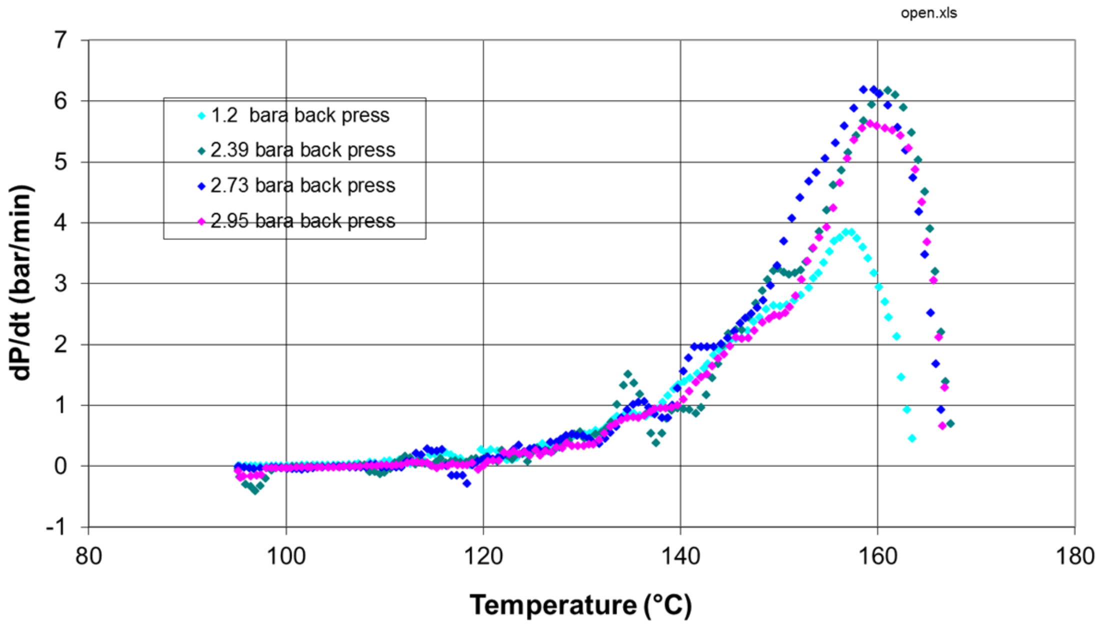

Figure 6 Open Systems Tests – Pressure rate versus Temperature

The conditions for the first series of pilot-scale experiments, which varied the fill level over four tests (p22, p25, p27 and p28), are shown in Table 1. The mass charged was varied from 78.5 kg in test p22 to 196 kg in test p28; the batch volume varied correspondingly.. Both variables are highlighted in italics in the table. The vent diameter was 75 mm for all tests and the dimensionless friction loss factor (4fL/D) was set to 1.5. The vent line is shown as a schematic in Figure 7.

Table 2 shows how the vent diameter and vent line friction was varied over three tests (pp02, pp03 and pp04) for the second series of experiments. Three vent lines of equal length were used (one for each test) but with different internal diameters and wall thickness (according to the pipe schedule). Vent diameters of between 49.2 mm (pp04) and 73.7 mm (pp02) were tested alongside friction loss factors of between 1.95 (pp02) and 2.29 (pp04). The effect of increased vent line friction is to reduce the available mass flux (G), see the Vent Sizing Annex. Data relating to the vent line is shown in italics in Table 2. The mass charged was 196.2 kg for all tests and subsequently the initial batch volume was always 250 dm^3. The vent line is shown as a schematic in Figure 8.

For both series of experiments the concentration of Trigonox 21, the concentration of the accelerator (NL49P) and the set pressures were kept constant.

Table 1 Experimental Conditions - Effect of Fill Level

Test number	**p22**	**p25**	**p27**	**p28**
Vent Diameter mm	75	75	75	75
4fL/D	1.5	1.5	1.5	1.5
Mass charged kg	***78.5***	***117.7***	***157***	***196.2***
Reactor Volume dm^3	340	340	340	340
Batch Volume dm^3	***100***	***150***	***200***	***250***
Trigonox 21 w/w %	20	20	20	20
Accelerator w/w %	1	1	1	1
Set Pressure bara	2	2	2	2

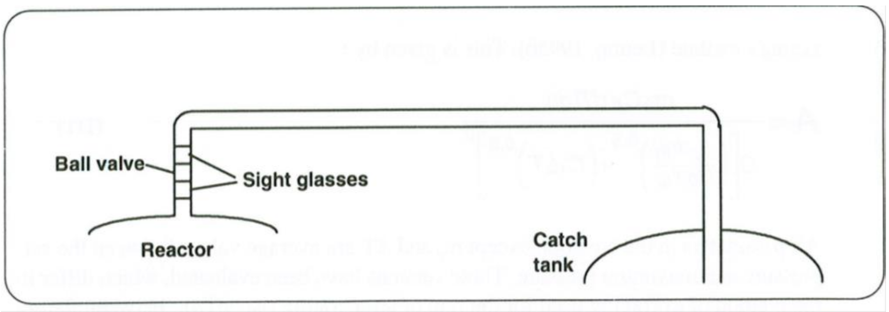

Figure 7 Vent Line Schematic - Effect of Fill Level

Table 2 Experimental Conditions - Effect of Vent Diameter

Test number	**pp02**	**pp03**	**pp04**
Vent Diameter mm	***73.7***	***62.7***	***49.2***
Flow area mm^2	***4261***	***3089***	***1905***
4fL/D	***1.95***	***2.05***	***2.29***
Mass charged kg	196.2	196.2	196.2
Reactor Volume dm^3	340	340	340
Batch Volume dm^3	250	250	250
Trigonox 21 w/w %	20	20	20
Accelerator w/w %	1	1	1
Set Pressure bara	2	2	2

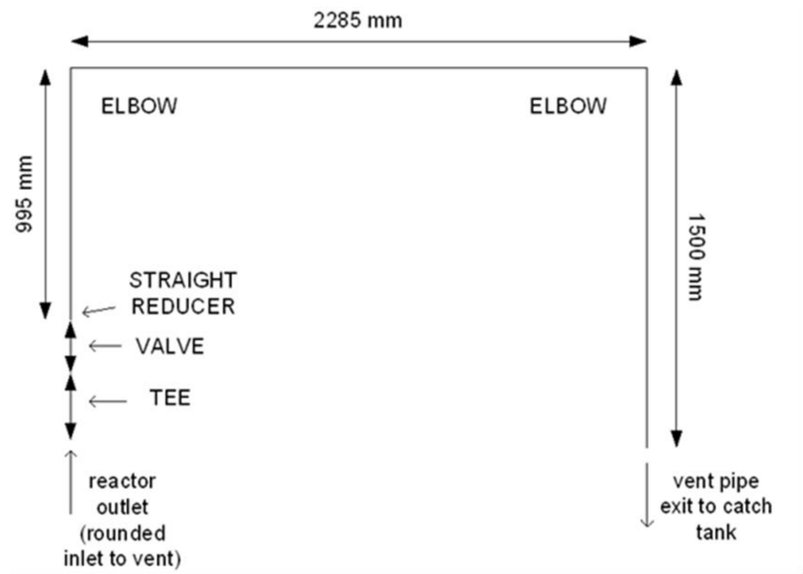

Figure 8 Vent Line Schematic Effect of Vent Diameter

Results and Vent Sizing – Comparison

Figures 9 and 10 show results for a typical pilot scale experiment pp04 (see Table 2). Figure 9 illustrates the reactor temperature and pressure plots. The temperature initially reduces due to mixing cold peroxide solution with the main bulk of solvent. As the reaction proceeds, the temperatures and pressure steadily increase until at just after 840s, the vent opens at the set pressure of 2 bara. The temperature continues to rise after vent opening until at 1200 s the gas generation is sufficient to swell the liquid to the top thermocouple in the vessel (TC01). A pressure peak then occurs due to the liquid level reaching the top of the vessel and leaving it via the vent. Figure 10 shows the vent line temperature plots, starting at 840 s, just before vent opening. Some two phase flow occurs just after vent opening, shown by similar vent line temperatures. After 1260s, there is again evidence of some two-phase flow because of similar vent line temperatures. Figure 2 shows the locations of the thermocouples (TC01 to TC05) within the reactor, vent line and catch tank system. The highest temperature was recorded by TC04 was 158.9°C.

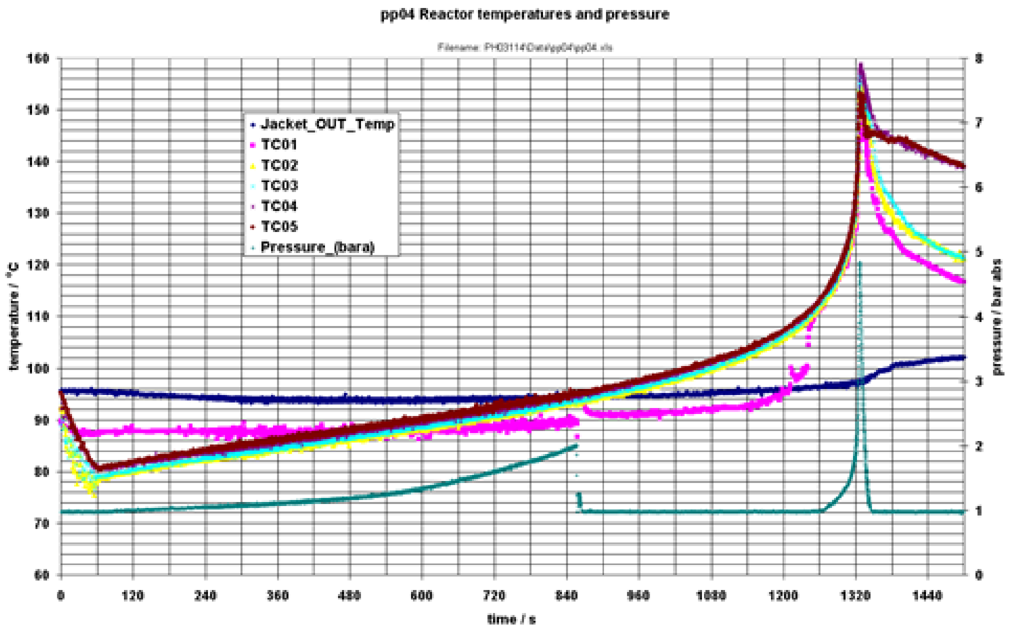

Figure 9 Reactor Temperatures and Pressures for Test pp04

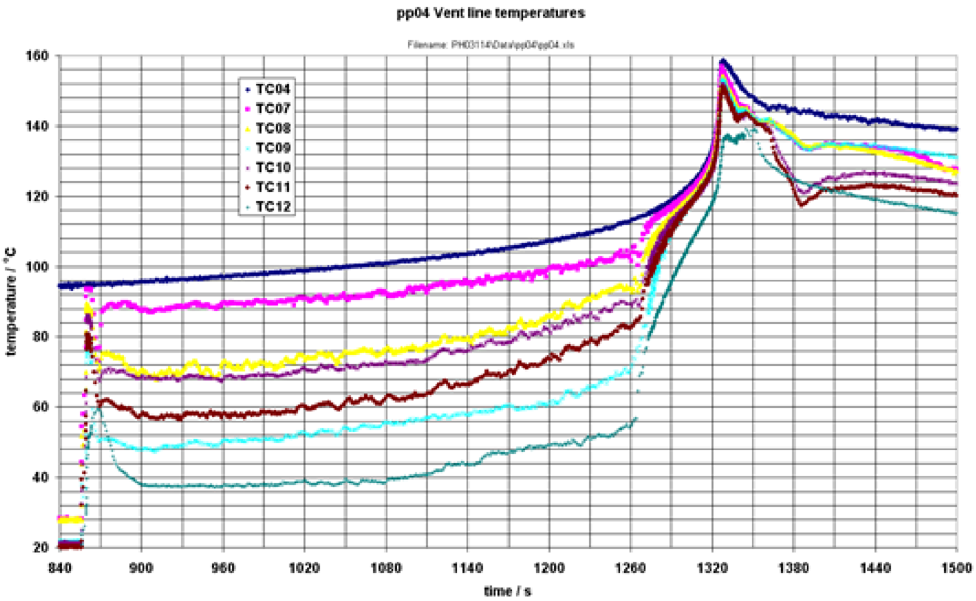

Figure 10 Vent Line Temperatures for Test pp04

Key Experimental Results

The three key experimental results are:

- The second maximum pressure peak (P_{max} (2nd Peak)) in the reactor, obtained directly from the pressure transducer;
- The mass in the reactor at the maximum pressure; and
- The maximum vent mass flow rate W_{max}.

The latter two were both estimated from the catch tank load cell data. Tables 3 and 4 show the effect of fill level and vent diameter respectively on the experimental results. The key experimental results are highlighted in italics in both tables. An important parameter in vent sizing is the void fraction, which is a measure of the free space in the reactor.

Table 3 Effect of Fill Level – Experimental Results

Test number	**p22**	**p25**	**p27**	**p28**
Vent Diameter mm	75	75	75	75
4fL/D	1.5	1.5	1.5	1.5
Mass charged kg	78.5	117.7	157	196.2
Set Pressure bara	2	2	2	2
Reactor Volume dm^3	340	340	340	340
Batch Volume dm^3	100	150	200	250
P_{max} (2nd Peak) bara	***1.20***	***2.39***	***2.73***	***2.96***
P_{max} mass kg	***71***	***84.4***	***91***	***92.7***
W_{max} kg/s	***0.91***	***6.17***	***10.68***	***12.78***

Table 4 Effect of Vent Diameter – Experimental Results

Test number	**pp02**	**pp03**	**pp04**
Vent Diameter mm	73.7	62.7	49.2
Flow area mm^2	4261	3089	1905
A/V m^{-1}	0.01253	0.00908	0.0056
4fL/D	1.95	2.05	2.29
Mass charged kg	196.2	196.2	196.2
Set Pressure bara	2	2	2
Reactor Volume dm^3	340	340	340
Batch Volume dm^3	250	250	250

P_{max} (2nd Peak) bara	***2.775***	***3.427***	***4.843***
P_{max} mass kg	***90.3***	***102.1***	***116.5***
W_{max} kg/s	***9.5***	***8.2***	***8.3***

Table 3 shows that the maximum pressure (P_{max} (2^{nd} Peak)) and the mass in the reactor at the maximum pressure (P_{max} mass) increase as the fill level rises. The larger the batch size, the more reactive material there is to generate higher pressures and give level swell. Table 4 shows that the maximum pressure (P_{max} (2^{nd} Peak)) decreases with increasing vent diameter and the mass in the reactor at the maximum pressure (P_{max} mass) also decreases with increasing vent diameter. The larger the vent size, the more easily material can escape through it, thus the maximum pressure is lower and there is less mass left in the reactor.

The experiments show the effects of both fill level and vent diameter on the maximum pressure produced in the pilot reactor. Vent sizing calculations give a predicted vent diameter, for a particular reaction mass and maximum pressure, which can be compared with actual vent diameter. If the calculated vent diameter is larger than the experimental vent, this is conservative. If the calculated vent diameter is less than the experimental vent diameter, this is not conservative. Some vent sizing methods take account of any mass loss prior to the maximum pressure, so it is useful to estimate the mass in the pilot reactor at this time, to compare with the calculations. An estimate of the maximum experimental mass flowrate is useful in evaluating vent sizing methods which calculate the mass flux G, the mass flowrate per unit area.

Numerical calculation - Vent Sizing

Vent sizing calculations were performed for the 4 experiments which varied the fill level and the 3 experiments which varied the vent diameter. The vent sizing calculations use the mass in the reactor and the experimental maximum pressure to calculate a vent diameter which can be compared with the experimental vent diameter. If the calculated vent diameter is larger than the experimental vent, this is safe. If the calculated vent diameter is less than the experimental vent diameter, this is unsafe. The various vent sizing equations used, their derivations and nomenclature can be found in the Vent Sizing Annex at the end of this paper. The initial mass in the reactor was used in the vent sizing and also 3 methods which take account of any transient mass loss prior to the maximum pressure. Either the experimental mass in the reactor at the maximum pressure could be used or 2 calculation methods which estimate the transient mass loss. Therefore the 4 approaches taken in the vent sizing were to:

1. Use the initial mass (i.e. no mass loss) based homogenous two-phase density to calculate W, G and the vent area A. The vent area was then compared with the experimental vent area by calculating the vent area ratio A_{calc}/ A_{exp}. This gives an indication of the over sizing or under sizing of the vent.
2. Use the mass at the experimental maximum pressure (Experimental P_{max} mass) based homogeneous two-phase density to calculate W, G and the vent area A. The vent area ratio A_{calc}/ A_{exp} was again calculated. An area reduction factor was also calculated by dividing the vent area calculated using the mass calculated at the experimental maximum pressure by the vent area calculated using Approach 1.
3. Calculate the reduced vent area using Leung's Transient Mass Loss equation (Equation 10). The vent area ratio A_{calc}/ A_{exp} was again calculated. An area reduction was again calculated by dividing the vent area calculated using the transient mass loss equation by the vent area calculated using Approach 1.
4. Calculate the area reduction factor K calculated by the Singh equation (Equation 12) which allows the reduced vent area to be calculated. The vent area ratio A_{calc}/ A_{exp} was again calculated.

A standard set of assumptions were used in the vent sizing: a mixture density (ρ_o) value of 703.3 kg/m^3 at 160°C was used to allow for liquid expansion rather than the initial mixture density of 784.9 kg/m^3 at 15°C. The test cell free volume (V) was set to 1.95 dm^3 to allow for space taken up by equipment in the calorimeter rather than the standard capacity of 3 dm^3. No temperature correction was made so that the temperature of the test cell (T_e) was assumed to be the same as the free space temperature (T_c).

Tables 5 and 6 summarise the vent sizing results showing the effect of fill level and vent diameter respectively. The degree of over sizing or under sizing can be seen in the ratio of the calculated vent area to the experimental vent area (A_{calc} to A_{exp}) which is highlighted in italics in both tables.

Taking experiment p25 as an example with a charge mass of 117.7 kg: the DIERS calculated vent area is 2.41 times the actual vent area and using the experimental mass at Pmax the DIERS calculated vent area is 1.5 times the actual vent area; both these calculated areas are safe. However the Leung Transient Mass loss calculated vent area is 0.82 times the actual vent area and the Singh Equation calculated vent area is 0.83 times the actual vent area; both these calculated vent areas are unsafe.

Now taking experiment pp04 as an example with a charge mass of 196.2 kg: the DIERS calculated vent area is 3.87 times the actual vent area, using the experimental mass at Pmax, the DIERS calculated vent area is 2.09 times the actual vent area, the Leung Transient Mass loss the calculated vent area is 1.91 times the actual vent area and the Singh Equation calculated the vent area is 1.34 times the actual vent area; all four of these calculated vent areas are safe..

Table 5 Effect of Fill Level – Vent Sizing Results

Test number	**p22**	**p25**	**p27**	**p28**
Mass charged kg	78.5	117.7	157	196.2
Vent Diameter mm	75	75	75	75
Calc Vent Diam mm (No mass loss)	181.73	116.50	127.50	132.19
Calc Vent Diam mm (P_{max} mass)	167.08	91.88	88.02	82.52
A_{calc} / A_{exp} ***(No mass loss)***	***5.87***	***2.41***	***2.89***	***3.11***
A_{calc} / A_{exp} ***(P_{max} mass)***	***4.96***	***1.5***	***1.38***	***1.21***
Area reduction factor (P_{max} mass)	0.85	0.62	0.48	0.39
Leung Equation (TML) (mm)	98.87	68.03	80.39	92.86
A_{calc} / A_{exp} ***(Leung TML)***	***1.74***	***0.82***	***1.15***	***1.53***
Area reduction factor Leung Equation (TML)	0.30	0.34	0.40	0.49
Singh Equation (mm)	106.9	68.53	75.00	77.76
A_{calc} / A_{exp} ***(Singh Equation)***	***2.03***	***0.83***	***1.00***	***1.07***
Area reduction factor Singh Equation	0.346	0.346	0.346	0.346

Table 6 Effect of Vent Diameter – Vent Sizing Results

Test number	**pp02**	**pp03**	**pp04**
Mass charged kg	196.2	196.2	196.2
Vent Diameter mm	73.7	62.7	49.2
Calc Vent Diam mm (No mass loss)	143.96	123.96	96.75
Calc Vent Diam mm (P_{max} mass)	87.75	83.24	71.16
A_{calc} / A_{exp} (No mass loss)	***3.82***	***3.91***	***3.87***
A_{calc} / A_{exp} (P_{max} mass)	***1.42***	***1.76***	***2.09***
Area reduction factor (P_{max} mass)	0.37	0.45	0.54
Leung Equation (TML) (mm)	101.13	87.08	67.97
A_{calc} / A_{exp} (Leung TML)	***1.88***	***1.93***	***1.91***
Area reduction factor Leung Equation (TML)	0.49	0.49	0.49
Singh Equation (mm)	84.68	72.92	56.91
A_{calc} / A_{exp} (Singh Equation)	***1.32***	***1.35***	***1.34***
Area reduction factor Singh Equation	0.346	0.346	0.346

Table 5 shows that the area reduction factor, based on the experimental mass at the maximum pressure, decreases with increasing fill level. Table 6 shows that the area reduction factor, based on the experimental mass at the maximum pressure, decreases with increasing vent diameter. Table 5 shows the effect of fill level and Table 6 the effects of vent size on the vent sizing results. Various comments can be made on the vent sizing methods: The standard (DIERS) vent sizing method oversized the vent by 3 to 4 times the vent area at high fill levels and significantly oversized the vent by 6 times at the lowest fill. Use of P_{max} mass with the DIERS method oversized the vent by 1.5 to 2 times the vent area at high fill levels and oversized the vent by 5 times at the lowest fill. However in practice a vent designer would not have the knowledge of the mass at the maximum pressure to take this approach.

Void Fractions

An important parameter in vent sizing is the void fraction, which is a measure of the free space in the reactor. Void fractions calculated using Equation 5 in the Vent Sizing Annex, with the batch volume (Vm) at both standard temperature (15°C) and the maximum reactor temperature (160°C), are shown in Tables 7 and 8. Two values are shown in the table one using the initial mass and one using the mass at the maximum pressure. The Leung Method (Leung,1992) was generally safe at the lowest and higher fills but potentially unsafe for experiment p25 (initial void fraction of 0.56 at 15°C and 0.51 at 160°C) suggesting a vent around 0.8 times the actual vent area. The Singh Method (1994) was generally safe at the lowest and higher fills but potentially unsafe for experiment p25 suggesting a vent around 0.8 times the actual vent area.

Table 7 Effect of Fill Level –Void Fractions

Test number	**p22**	**p25**	**p27**	**p28**
Mass charged kg	78.5	117.7	157	196.2
Vent Diameter mm	75	75	75	75
Initial Void fraction at 15°C	0.71	0.56	0.41	0.26
Initial Void fraction at 160°C	0.67	0.51	0.34	0.18
P_{max} Void fraction at 15°C	0.73	0.68	0.66	0.65
P_{max} Void fraction at 160°C	0.70	0.65	0.62	0.61

Table 8 Effect of Vent Diameter –Void Fractions

Test number	**pp02**	**pp03**	**pp04**
Mass charged kg	196.2	196.2	193
Vent Diameter mm	73.7	62.7	49.2
Initial Void fraction at 15°C	0.26	0.26	0.26
Initial Void fraction at 160°C	0.18	0.18	0.18
Pmax Void fraction at 15°C	0.66	0.62	0.56
Pmax Void fraction at 160°C	0.62	0.57	0.51

Figure 11 shows the void fraction at the maximum pressure versus the initial void fraction for both series of experiments. The void fractions have been calculated using the liquid density at 15°C, Not Expansion Corrected (NEC) and 160°C, Expansion Corrected (EC). The curve shown in Figure 11 is the void fraction at the maximum pressure calculated using Leung's Equation (11) for transient mass loss, i.e. void fraction to the 0.5 power.

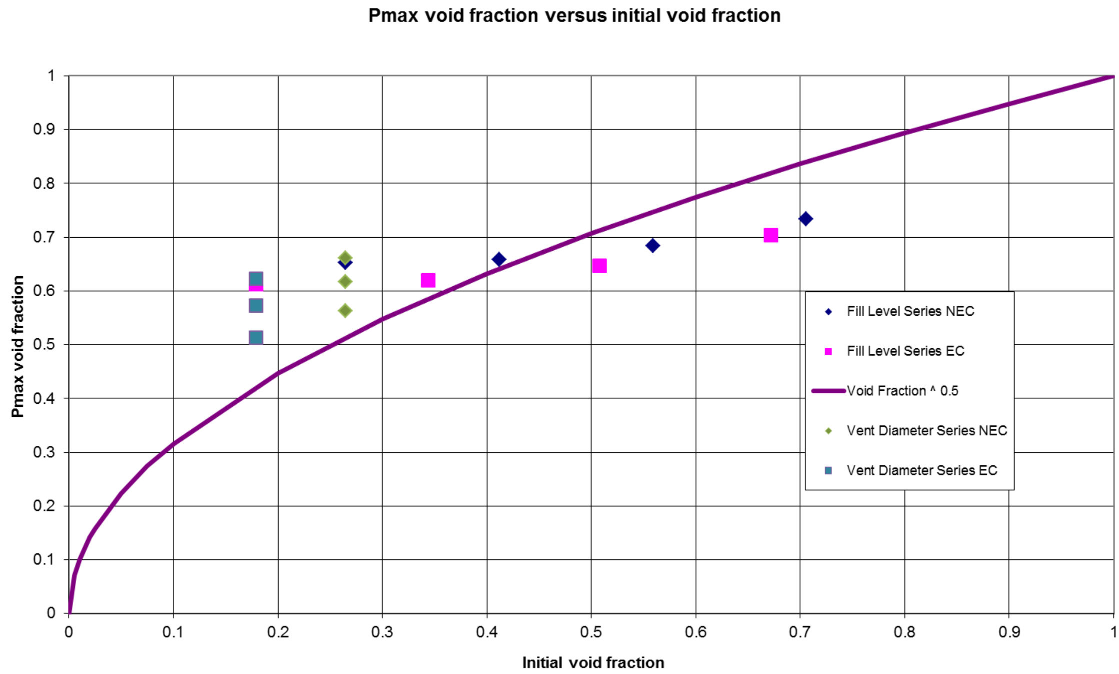

Figure 11 Void fraction at maximum pressure versus initial void fraction

Figure 12 shows the area reduction factor (ARF) calculated using the experimental mass in the reactor at the maximum pressure versus the initial void fraction for both series of experiments. The void fractions have been calculated using the liquid density at both 15°C (NEC) and 160°C (EC). The curve shown in Figure 12 is the area reduction factor calculated using Leung's Equation for Transient Mass Loss.

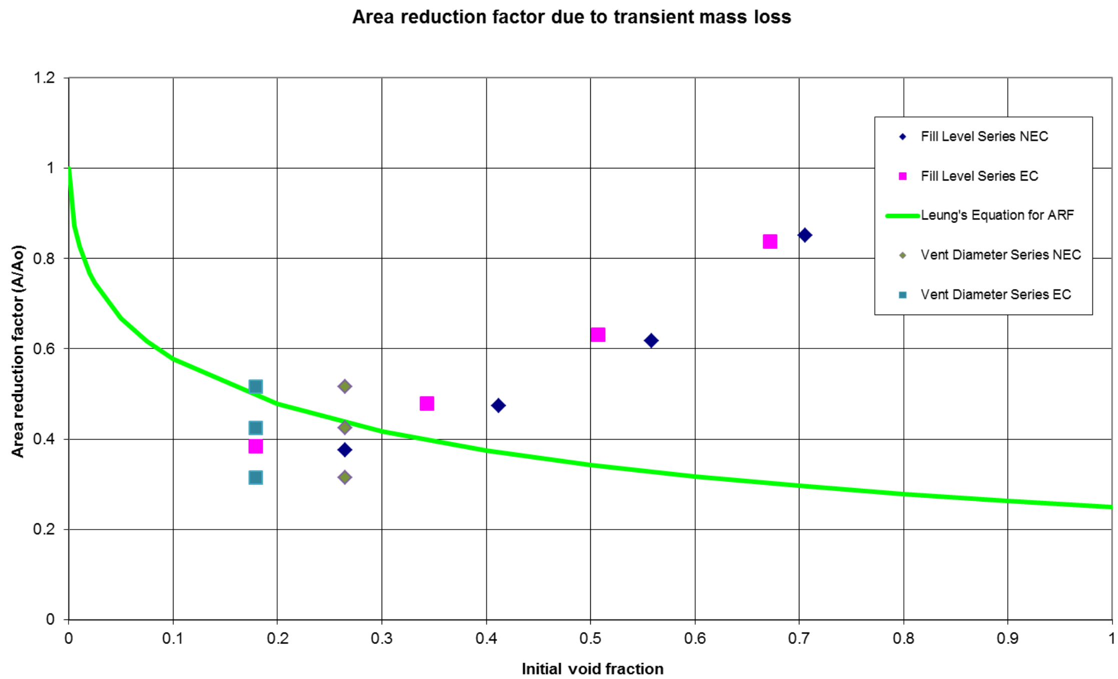

Figure 12 Area reduction factor due to transient mass loss

Figure 11 shows that the observed void fraction at the maximum pressure increases linearly with initial void fraction. Leung suggested that the void fraction at the maximum pressure would vary with the initial void fraction to the 0.5 power. Figure 12 shows that the observed area reduction factor (based on the mass in the reactor at the maximum pressure) increases with initial void fraction. The Leung area reduction factor seems to be only representative at low initial void fractions (i.e. higher fill levels). Leung thought that area reduction factor would decrease with initial void fraction.

This helps to explain the Transient Mass Loss vent sizing. The Transient Mass Loss approach works for low void fractions (high fill levels) that is for experiments p27, p28, pp02, pp03 and pp04; but not for high void fractions (low fill levels). For the highest void fraction (low fill level) experiment p22, the Transient Mass Loss approach works only because the flow is largely single phase flow. Single phase flow is suggested by the low 2nd pressure peak (P_{max}) at 1.20 bara, the low experimental mass flowrate (W_{max}) at 0.91 kg/s and the low back calculated density (W_{max}/Q_{gmax}) at 5 kg/m^3. For intermediate void fractions (0.56 or 0.51), experiment p25 the vent is undersized.

Density Estimations

An important factor in vent sizing is the two phase density of the venting mixture, which accounts for both the liquid and gaseous components. Thus the two phase density is not the same as the liquid density. The DIERS vent sizing methods assume homogeneous vessel venting; where the two phase density is calculated as the mass in the reactor divided by the reactor volume. Three values were available for the two phase density of this mixture. Firstly the homogeneous density calculated using the initial mass divided by the reactor volume. Secondly the homogeneous density calculated using the mass at the maximum pressure divided by the reactor volume. Thirdly the back calculated density from the maximum vent mass flow rate W_{max} divided by the maximum volumetric gas evolution rate at the maximum pressure Q_{gmax}. Tables 9 and 10 provide the density estimations for the experiments on the effect of fill level and effect of vent diameter respectively.

Table 9 Effect of Fill Level – Density Estimations

Test number	**p22**	**p25**	**p27**	**p28**
Mass charged kg	78.5	117.7	157	196.2
Vent Diameter mm	75	75	75	75
Homogeneous density initial mass (kg/m^3)	231	346	462	577
Homogeneous density P_{max} mass (kg/m^3)	209	248	268	273
Back calculated Density (W_{max}/Q_{gmax}) (kg/m^3)	5	58	104	135

Table 10 Effect of Vent Diameter – Density Estimations

Test number	**pp02**	**pp03**	**pp04**
Mass charged kg	196.2	196.2	193
Vent Diameter mm	73.7	62.7	49.2
Homogeneous density initial mass (kg/m^3)	577	577	577
Homogeneous density P_{max} mass (kg/m^3)	266	300	343
Back calculated Density (W_{max}/Q_{gmax}) (kg/m^3)	96	89	112

Tables 9 and 10 compare the densities estimated in various ways, in terms of the effects of fill level and vent diameter, respectively. Homogeneous densities were calculated with and without mass loss. The Homogeneous density with mass loss increases with increasing fill level and increases with decreasing vent diameter. Observed densities are significantly lower than with homogeneous assumption. These lower observed densities may account for oversizing.

Use of Simplified Vent Sizing Equations

In order to better explain the venting of a gassy system a simplified approach was developed to show the calculation of vent area. Equation (17) is simplified because it does not account for back pressure or vent line friction. The derivation of equation (17) can be found in the Vent Sizing Annex at the end of this paper. The simplified equation for vent area was then rearranged in equation (18) to show the effects on maximum pressure of various changes in variables.

$$A_o = Q_{gmax} (\rho_f / P_{max})^{1/2} ((1-\alpha_0)^{1/2} / G_c^*) \quad (17)$$

$$P_{max} = ((Q_{gmax}/A_o) (\rho_f)^{1/2} ((1-\alpha_0)^{1/2} / G_c^*))^2 \quad (18)$$

The effects of changes in variables on the maximum pressure P_{max} can now clearly be seen from equation (18):

- It is strongly dependent on the volumetric gas generation rate Q_{gmax} and increases with it.
- It is strongly dependent on the vent area A and decreases with it.
- It is weakly dependent on the liquid density ρ_f and increases with it.
- It is dependent on the initial void fraction which appears directly in equation (18) and G_c^* is also a complex function of void fraction.

The influence of void fraction on the maximum pressure P_{max} is shown by the value of the dimensionless group $((1-\alpha_0)^{1/2} / G_c^*))^2$ named Hare's Gassy Dimensionless Group which is plotted in Figures 13 and 14 as a function of void fraction. Figure 13 shows the experiments which varied the fill level and Figure 14 shows the experiments which varied the vent diameter. In both figures the magenta and blue squares show the initial void fractions (ivf) and the yellow and cyan diamonds show the void fractions at the maximum pressure (pmvf) at both 15°C and 160°C.

The experiments showed that the maximum pressure was strongly dependent on the vent area and decreased with it. Figure 13 considers the effect of fill level; it shows there was a larger range of initial void fractions but a smaller range of void fractions at the maximum pressure. Figure 14 considers the effect of vent diameter; all the tests had the same initial void fraction so the void fraction variation at the maximum pressure was due to the effects of vent diameter. The Figures show that maximum pressure decreases with void fraction α_o provided $\alpha_o > 0.3$ and increases with void fraction provided $\alpha_o < 0.3$.

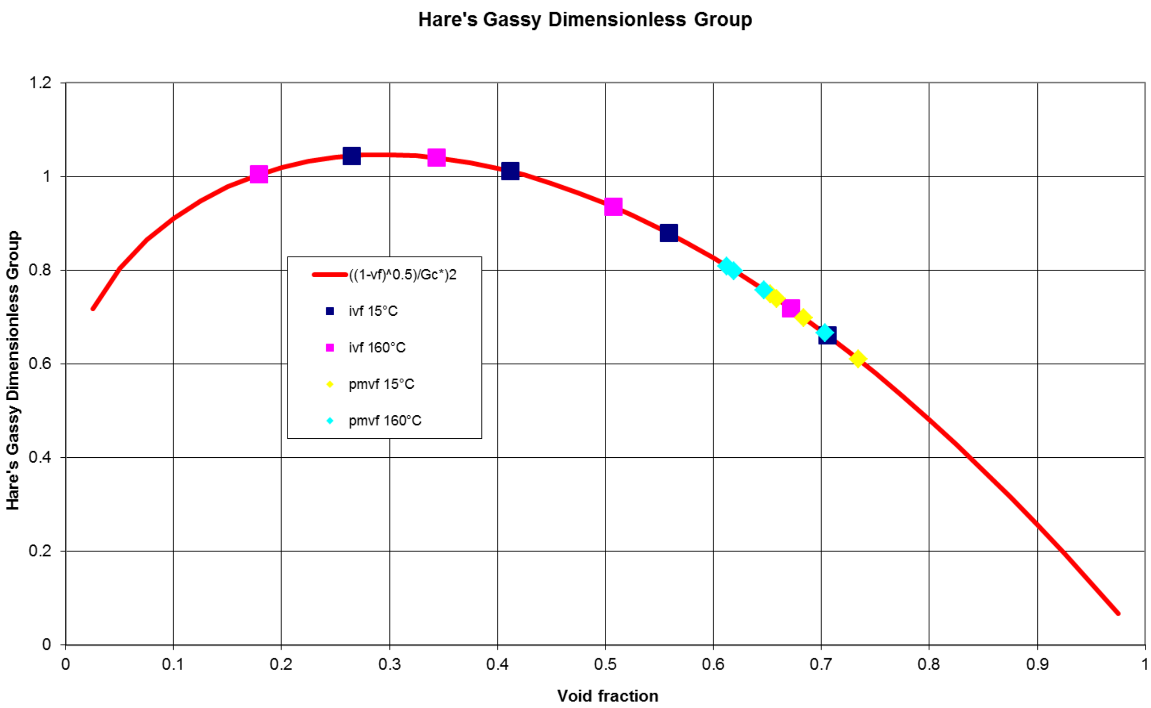

Figure 13 Effect of vessel fill - Calculating maximum pressure

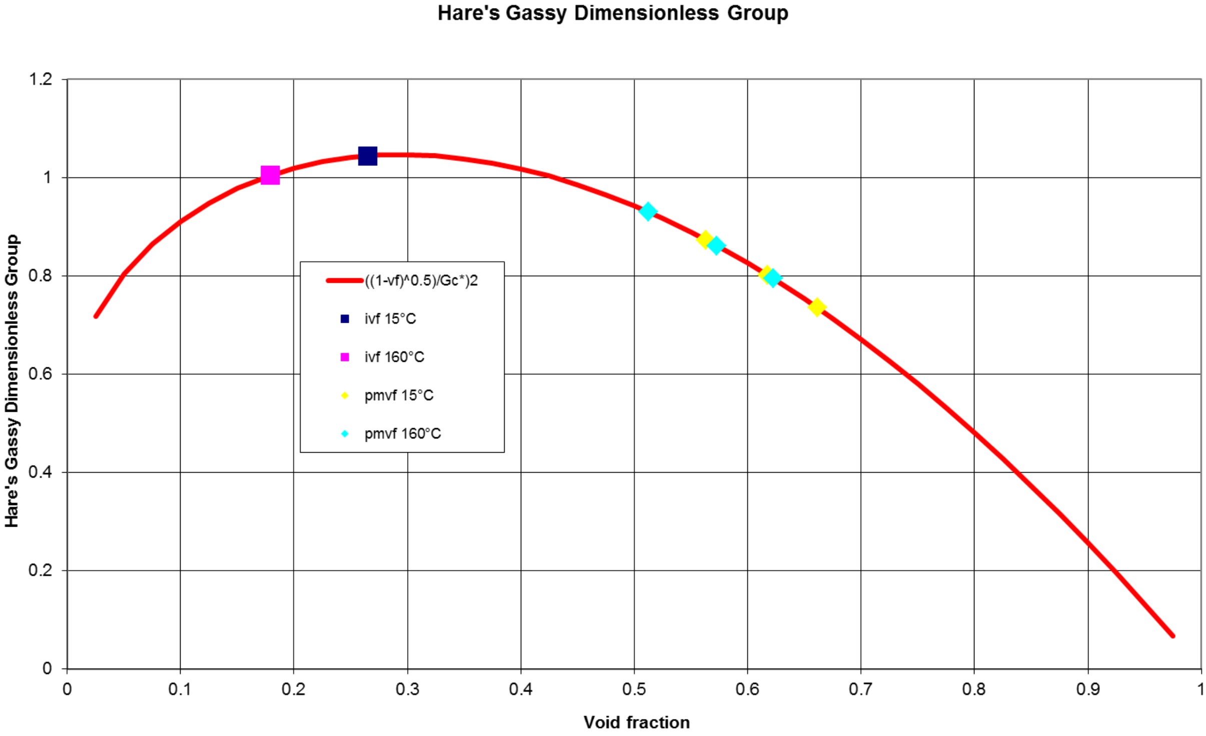

Figure 14 Effect of vent diameter -Calculating maximum pressure

To aid interpretation of the experiments and assess the suitability of the various vent sizing methods, options for further analysis could include:

- Interpretation of mass flow and mass flux data;
- Level swell calculations, to better account for disengagement and to explore the churn turbulent flow regime;
- Simplified Vent Sizing Methods, to include the effect of friction, back pressure and transient mass loss; and
- Computer models.

Conclusions

The main conclusions are as follows:

- Pilot scale experimental results and vent sizing calculations have been presented on a gassy runaway reaction system showing the effects of varying the fill level and vent size;
- The DIERS gassy method is conservative because it was found to oversize the vent;
- Data on the mass in the reactor at the maximum pressure showed, that in principle, the DIERS gassy approach is reasonable; and
- Methods which reduce the DIERS vent area, such as those by Leung and Singh, can be unsafe at certain initial fill levels (void fractions around 0.56 or 0.51).
- Options for further analysis are given.

Nomenclature

Phi Tec Data:

$(dP/dt)_{max}$	maximum rate of pressure rise (Pa/s)
P_e	corresponding pressure (Pa)
T_e	corresponding temperature (K)
$(dT/dt)_e$	corresponding temperature rate (K/s)

m_e	initial sample mass (kg)
V	free space volume (m^3)
T_c	free space temperature (K)
Q_{gemax}	volumetric gas evolution rate at P_e (m^3/s)
$(dP/dt)_v$	rate of pressure rise at vent opening (or at level swell) (Pa/s)

Real reactor data:

m	mass in reactor (kg)
P_{max}	maximum pressure (Pa)
V_R	reactor volume (m^3)
G	mass flux corrected for friction and back pressure (kg/m^2 s)
Q_{gmax}	volumetric gas evolution rate at P_{max} (m^3/s)
A_o	vent area (m^2)
G_c	critical mass flux (kg/m^2 s)
α_o	initial void fraction
V_m	batch volume (m^3)
κ	isentropic coefficient
ω	omega
G_c*	dimensionless mass flux
ρ_o	initial two phase density (kg/m^3)
η_c	critical pressure ratio
$(G/G_c)_{friction}$	mass flux friction correction factor
$(G/G_c)_{backpressure}$	mass flux back pressure correction factor
$4fL/D$	term that correlates with frictional pressure loss
f	Fanning Friction
L	equivalent length of vent line (m)
D	relief system diameter (m)
K	Singh area reduction factor
W	required two phase relief rate kg/s
W_{max}	maximum vent mass flow kg/s
A_{calc}/A_{exp}	vent area ratio (calculated to experiment)

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Acknowledgments

Tim Snee led the experiments on the effect of fill level and Jake Kay led the experiments on the effect of vent diameter. The open system adiabatic tests were carried out by Diane Kerr. Their contribution to the work is gratefully acknowledged.

Disclaimer

The work described in this paper was funded by the Health and Safety Executive. The opinions and conclusions are those of the author and do not reflect HSE policy. The vent sizing calculations are also based on one typical open system test and the assumption that the system is gassy and not hybrid. Tim Snee and Jake Kay were relied on for the interpretation of pilot scale load cell data. Note for the second series of experiments, the active ingredient (Cobalt Octoate) in the NL 49P accelerator, was dissolved in a different solvent.

Vent Sizing Annex

This annex outlines the equations used for vent sizing. Equations are taken from Etchells and Wilday (1998) except where otherwise indicated.

Standard Vent Sizing Equations – Vent Area

The volumetric gas evolution rate Q_{gemax} is calculated from the small scale adiabatic maximum rate of pressure rise $(dP/dt)_{max}$ with corresponding pressure P_e and temperature T_e.

$$Q_{gemax} = [((V/P_e)(dP/dt)_{max}) - ((V/T_e)(dT/dt)_e)] [(T_e/T_c) (m/m_e)] \qquad (1)$$

For the open system tests, the corresponding temperature will be greater than the free space temperature T_c (i.e. $T_e>T_c$) and the change in corresponding temperature will be small i.e. $(dT/dt)_e = 0$. Therefore equation (1) can be simplified as:

$$Q_{gemax} = (V/P_e) (dP/dt)_{max}) (T_e/T_c) (m/m_e) \qquad (2)$$

The volumetric gas evolution rate Q_{gmax} is then calculated at the maximum pressure P_{max} in the real reactor.

$$Q_{gmax} = Q_{gemax} (P_e / P_{max}) \qquad (3)$$

The DIERS vent area A_V is then calculated using the mass in the real reactor m, the reactor volume V_R and the mass flux G corrected for friction and back pressure.

$$A_o = (Q_{gmax} / G) (m / V_R) \qquad (4)$$

Standard Vent Sizing Equations - Mass Flux

In equation (4), the mass flux has also to be calculated. The Omega method will be used which involves the calculation of a dimensionless mass flux G_c* which is then corrected for vent line friction and back pressure. Firstly the initial void fraction α_o is calculated from the reactor volume V_R and batch volume V_m:

$$\alpha_o = (V_R - V_m) / V_R \qquad (5)$$

Secondly Omega for a gassy system is calculated using the initial void fraction and the isentropic coefficient κ:

$$\omega = \alpha_o / \kappa \qquad (6)$$

Thirdly the initial two phase density is obtained using the mass in the reactor and the reactor volume:

$$\rho_o = m / V_R \qquad (7)$$

The dimensionless mass flux G_c* is then calculated using the Omega value. Charts for obtaining G_c* are available in Etchells and Wilday (1998). Next the choked mass flux is calculated for the nozzle:

$$G_c = G_c^* (P_{max}\, \rho_0)^{1/2} \qquad (8)$$

Next the corrected mass flux G is obtained using the friction $(G/G_c)_{friction}$ and back pressure $(G/G_c)_{backpressure}$ correction factors:

$$G = G_c (G/G_c)_{friction} (G/G_c)_{backpressure} \qquad (9)$$

Leung Transient Mass Loss Equations

Leung (1992) proposed an equation which allowed a reduced vent area (A_m) to be calculated from the DIERS vent area (A_o) to take account of the mass loss on vent opening. Note the Leung Transient Mass Loss equation given in Etchells and Wilday (1998) is incorrect but the correct version is given below.

$$A_m = A_o (1/(1+\alpha_o^{1/2})^2) \qquad (10)$$

Leung's assumption was that the void fraction (α_m) at the maximum pressure was related to the initial void fraction α_o by the equation:

$$\alpha_m = \alpha_o^{1/2} \qquad (11)$$

Singh Equation for gas-generating runaway reactions

Singh (1994) proposed an area reduction factor K which reduces the DIERS vent sizing area by taking account of the rate of pressure rise at vent opening $(dPdt)_v$ (or when level swell first causes two-phase venting), as well the maximum rate of pressure rise $(dP/dt)_{max}$:

$K = 1 + 2([1-(dPdt)_v/(dP/dt)_{max}]/ [1+(dPdt)_v/(dP/dt)_{max}])$ (12)

For the system considered the level swell was indicated in Figure 6 by a change in the pressure gradient at a temperature of120°C when the adiabatic pressure rate was 0.189 bar min. The maximum adiabatic pressure rate was 6.58 bar/ min at a temperature of 159.6 °C.

Simplified Vent Sizing Equations

In order to better explain the venting of a gassy system a simplified approach was developed to show the calculation of vent area. The equation is simplified in that it does not account for back pressure or vent line friction. The simplified equation for vent area was then rearranged to show the effects on maximum pressure of various changes in variables.

The DIERS Vent Sizing Equation for vent area A_o is shown below:

$A_o = (Q_{gmax} / G) (m / V_R)$ (13)

Choked mass flux for a nozzle G_c can be calculated using the Omega method as:

$G_c = G_c^* (P_{max}\ \rho_0)^{1/2}$ (14)

Substituting the G_c value from equation (14) into (13) gives the first equation for the vent area A:

$A = (Q_{gmax} (\rho_o / P_{max})^{1/2}(1/G_c^*)$ (15)

The two phase density ρ_o can be calculated using the void fraction α_o and liquid phase density ρ_f:

$\rho_0 = (1-\alpha_o)\ \rho_f$ (16)

Substituting the ρ_o value from equation (16) into (15) gives the second equation for the vent area A_o:

$A_o = Q_{gmax} (\rho_f / P_{max})^{1/2} ((1-\alpha_0)^{1/2} / G_c^*)$ (17)

Equation (17) for vent area A_o can be rearranged to give an equation for the maximum pressure P_{max}

$P_{max} = ((Q_{gmax}/A_o) (\rho_f)^{1/2} ((1-\alpha_0)^{1/2} / G_c^*))^2$ (18)