Runaway System Characterization and Vent Sizing Based on DIERS Methodology

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This article reveals the diverse nature of runaway systems as well as some general trends. In addition, it also serves to point out the usefulness of such an apparatus in characterizing virtually unknown systems

INTRODUCTION

A bench-scale apparatus for characterizing runaway reactions has been developed as part of an extensive R&D program of AIChE's Design Institute for Emergency Relief Systems (DIERS). While previous publications have dealt with its capability [1] and the thermal data acquisition [2] aspects, the present paper focuses on its application in vent sizing for some fifty industrial chemical systems tested in the last two years following completion of the DIERS program. These systems encompass a wide spectrum of the chemical processing industry with more than twenty U.S. companies represented. Because of the proprietary nature of most of these studies, the systems are grouped into several general categories without reference to a particular recipe.

SYSTEM CLASSIFICATION

Runaway reaction systems can generally be classified as tempered or non-tempered systems. A tempered system is one in which the reaction heat can be removed by latent heat of vaporization, thus any significant further temperature rise is prevented. Many of these systems are in fact normally operated in the refluxing mode for temperature control. The latent heat can be provided by either the reactant or the solvent. For this reason these systems typically possess high vapor pressure even at ambient temperature. Note that a tempered reaction can accommodate a "gassy" reaction (i.e., reaction that gives off gases) as long as the reaction temperature can be controlled. Low concentration hydrogen peroxide is an example of a tempered but gassy reaction. On the other hand, a non-tempered system exhibits little or no latent heat of cooling, thus is typical of a low vapor pressure system. In this case, the heat release is largely retained in the runaway charge which can lead to peak temperature rise rate and gas/vapor generation rate.

Because the vent sizing methodology (as discussed in the next section) differs depending on the type of system encountered, it is prudent to make such a delineation first by the following tests:

1. From a closed system test, a tempered reaction without gas evolution normally yields a linear relationship of pressure-temperature data on a Cox chart plot (i.e., log pressure versus reciprocal temperature).
2. From an open system test, a tempered reaction is evident by an abrupt halt in temperature rise corre-

sponding to the saturation temperature at the containment pressure (which is usually kept at the relief set pressure). This technique works well when the reaction rate is relatively low, say, self-heat rate less than 10°C/min. Above this rate, it is difficult to judge whether the tempering condition is still being maintained since the rapid composition change will invariably cause a continuous shift in the pressure-temperature [or vapor-liquid equilibrium (VLE)] relationship. Typically, this translates to a gradual rise in tempering temperature. When such a situation occurs, test method (3) below is recommended.
3. From a flow regime test (top venting test), a tempered system will exhibit an early turnaround in temperature simultaneous with the depressurization. It is this turnaround behavior due to latent heat of cooling that is being counted on in the vent sizing methodology for tempered systems.

To assure long-term tempering, the reaction should be allowed to go to completion while maintaining a constant containment pressure kept at (a) relief set pressure for a safety relief valve (SRV) of the reclosure type or (b) ambient pressure for a ruptured disk or a SRV of the nonclosure type. An exception to such a test would be for a foamy system where the reactor vessel is expected to be essentially empty a relatively short time after relief venting.

OVERVIEW OF VENT SIZING METHODOLOGY

The vent sizing methodology is based on the premise that two-phase flow will enter the relief vent line and the vessel content will behave as a homogeneous two-phase mixture. The design methods are summarized below.

TEMPERED/VAPOR SYSTEM (Type Ia)

Method:

1. Generalized vent sizing nomograph [3] (based on a turnaround pressure of 120% of the absolute pressure).
2. Simplified equations allowing a broad range of overpressure [4].

Both methods are based on turbulent flashing flow conditions approximated by the homogeneous equilibrium flow model [5, 6]. For viscous laminar flow conditions, the experimentally measured G valve should be used [1].

TABLE 1. SUMMARY OF SYSTEMS TESTED AND THEIR VENT SIZES

Sys. No.	Identification	Relief Set $P_{set}(T_{set})$	Sys. Type	Self-Heat Rate °C/min at Set	Vent Area m² per 1000 kg (%OP)	Specific Comments
1	Phenol-HCHO-Caustic	15 psig (130 ± 5°C)	I	70	0.16 (28%)	Process temperature 40°C
2	Phenol-HCHO-Caustic	5 psig (115°C)	I	10-150	0.01-0.13 (100%)	Low range reflects controlled addition.
3	Phenol-HCHO-Caustic	15 psig (125°C)	I	50-500	0.04-0.4 (20%)	Upper range reflects catalyst mischarge.
4	Phenol-HCHO-Caustic	100 psig (179°C)	I	2	3×10^{-4} (20%)	37.5% HCHO, simulate external heating at 2°C/min.
5	Styrene-BPO	30 psig (130°C)	I	12	0.005 (20%)	Dilute styrene,
6	Styrene Solution	300 psig	I	<0.1	—	P_{max} <300 psig.
7	1,3 Butadiene	150 psig (85°C)	I	0.3-3	4×10^{-5}-4×10^{-4} (20%)	Emulsion polymerization with Redox agent.
8	1,3 Butadiene	500 psig (145°C)	I	13	4×10^{-4} (10%)	Bulk polymerization with peroxide.
9	Vinyl Acetate	30 psig (105°C)	I	<0.1	—	$P_{max} \simeq 24$ psig, emulsion polymerization.
10	Vinyl Acetate	30 psig (105°C)	I	1000	0.7 (30%)	Bulk polymerization with BPO.
11	Chlorobutadiene Isomer	30 psig (105°C)	I	0.15	8×10^{-5} (10%)	Distillation operation.
12	Dichlorobutadiene	50 psig (185°C)	I	300	0.08 (15%)	Uninhibited monomer.
13	Methyl Methacrylate Mix	25 psig (131°C)	I	0.3-170	8×10^{-5}-0.07 (20%)	Upper range reflects solvent mischarge and double initiator.
14	Acrylate Monomer Mix	15 psig (110°C)	I	17-2000	0.01-1.5 (20%)	Upper range reflects solvent mischarge.
15	Furfuryl Alcohol Soln.	15 psig (125°C)	I	0.3-20	2×10^{-4}-0.014 (20%)	Upper range reflects double catalyst charge.
16	ACN-Diisobutylene-H_2SO_4	30 psig (110°C)	I	3.5	1.6-10^{-3}(20%)	
17	Acrylic Acid-PO-TEA	30 psig (190°C)	I	2.5	6.5×10^{-4} (20%)	P_{max} only 45 psig.
18	HCHO-Acetone-Caustic	12 psig (107°C)	I	1000	1.5 (20%)	First reaction very energetic, second one more mild.
19	HCHO-Acrylamide-Caustic	30 psig	I	<0.1	—	$P_{max} < P_{set}$.
20	Acetone-Sugar-HCHO	5 psig (109°C)	I	0.1	1×10^{-4} (100%)	Decomposition reaction with slight gas evolution.
21	Triallycyanurate	40 psig	II	>200	>0.07 (150%)	Direct scaling, P_{max} > MAWP, monomer has low vapor pressure.
22	EPI-Base Resin	5 psig (100°C)	I	<0.1	—	$P_{max} < P_{set}$.
23	Epoxy Resin	160 psig	II	30	3.6×10^{-3} (0%)	Direct Scaling, $Q_{max} \simeq 0.22$ m³/s per 1000 kg charge.
24	Epi-Mix-Caustic	50 psig (156°C)	I	1	4×10^{-4} (20%)	External heating during runaway little reaction at set.
25	Epi-Bisphenol	0.2 psig (108°C)	I	1.5	0.058 (70%)	MAWP 0.4 psig.
26	Epi-Resin-Caustic	0.2 psig (108°C)	I	0.5	5×10^{-3} (70%)	Small amount of gas evolution.
27	PO-Acrylic Acid-Catalyst	300 psig (171°C)	I	100	4×10^{-3} (15%)	Slight amount of gas evolution.
28	EO-Acrylic Acid-Catalyst	300 psig (122°C)	I	300	8×10^{-3} (30%)	No gas evolution detected.
29	Hydrogen Cyanide	8 psig (40°C)	I	1.5	1.2×10^{-3} (50%)	Polymerization reaction needs to be quenched upon blowdown.
30	PO-Catalyzed Crude	105 psig (135°C)	I	5.5	1×10^{-3} (20%)	Polyether reaction.
31	Dicyclopentadiene-1,3 Butadiene	350 psig	II	600	6×10^{-3} (10%)	Direct scaling, no sign of gas evolution.
32	Peracetic Acid-Cyclohexanone	44 psig (140°C)	I	22	4.2×10^{-3} (40%)	Parallel reaction with one being decomposition type.
33	Cumene Hydroperoxide	4 psig (163°C)	I→II	1.5 → 200	2×10^{-3}-0.4 (50%)	Tempered system at low conc., non-tempered at high conc.
34	t-Butyl Hydroperoxide	100 psig (172°C)	I	8.5	1.4×10^{-3} (10%)	Reaction showed a later exotherm if allowed to sustain at set pressure >30 minutes.
35	Dipropylene Glycol Methyl Ether	35 psig	II	>600	$>4 \times 10^{-3}$ (−)	P_{max} > 135 psig via direct scaling.
36	3-Methyl Mercapto Propanol	60 psig	II	~100	2.8×10^{-3} (0%)	Q_{max} = 0.1 m³/s per 1000 kg charge, low vapor pressure.
37	Monoethanol Amine	25 psig (210°C)	I	0.5	4.8×10^{-4} (10%)	Reaction heat small compared with external heating.
38	Diazonium Salt-HF	10 psig (~50°C)	I	1000 (Peak)	0.073	Direct simulation, $P_{max} \simeq 7$ psig during venting.

39	Malathion Crude	60 psig, est.	II	250 (Peak)	1.4×10^{-3} (110%)	Direct simulation, P_{max} = 125 psig during venting.
40	Peri Acid-Sodium Nitrite-H_2SO_4	50 psig	?	5 (Peak)	5.5×10^{-4}	Q_{max} = 0.005 m^3/s per 1000 kg charge.
41	Process A	100 psig	II	>2000 (Peak)	>0.015	Direct simulation P_{max} > 200 psig during venting.
42	Process B	75 psig	II	~100 (Peak)	0.01	Direct simulation $P_{max} \simeq 6$ psi above back pressure.
43	Process C	25 psig	II	1800	0.17	Q_{max} = 5.7 m^3/s per 1000 kg charge, distillation process.
44	Process D	25 psig (−12°C)	I	2	1.4×10^{-3} (30% OP)	Alkylation with 3-bromocylohexene.
45	Process E	30 psig (157°C)	I	9	2.5×10^{-3} (30% OP)	LAH reduction of intermediate with gas evolution.
46	Process F	13 psig (80°C)	I	27	5×10^{-3} (100% OP)	Sodium borohydride reduction of an ester with gas evolution.
47	Process G	13 psig (100°C)	I	0.2	3.3×10^{-4} (0% OP)	Free radical reaction using AIBN.
48	Thionyl Chloride-Benzyl Alcohol	15 psig	II	—	3.4×10^{-4} (0% OP)	Controlled addition, Q_{max} = 0.004 m^3/s per 1000 kg.
49	Trinitroglycerin (Paste)	25 psig	II	—	5.5×10^{-4}-0.015	Q_{max} = 0.01 to 0.28 m^3/s per 1000 kg.
50	Trinitroglycerin (Powder)	25 psig	II	—	—	Explosive Runaway resembling detonation.
51	p-Nitrophenyl-hydrazine-DMSO	25 psig (224°C)	I	55	0.012 (20% OP)	Without solvent, direct scaling yields 1.1 m^2/1000 kg.
52	p-Diisopropylbenzene Monohydroperoxide	10 psig	II	3000 (Peak)	0.18	P_{max} = 70 psig via direct scaling.
53	Methoxyamine Hydrochloride-Butanol	25 psig (130°C)	I	0.6	6.3×10^{-4} (20% OP)	Without solvent nontempered system, no data
54	o-Nitrobenzoyl Acid-Thionyl Chloride	25 psig	II	10,000	0.35 (P_{max} 200 psig)	Too energetic to be vented safely.
55	Hydroxylamine Sulfate	25 psig	II	—	—	Explosive runaway resembling detonation.

Abbreviations: Type I = Tempered system.
Type II = Nontempered system.
AIBN = Azobisisobutyronitrite.
BPO = Benzoyl peroxide.
DMSO = Dimethyl Sulfoxide.
EO = Ethylene oxide.
Epi = Epichlorohydrin.
HCHO = Formaldehyde.
HF = Hydrogen fluoride.
LAH = Lithium aluminum hydride.
MAWP = Maximum allowable working pressure.
PO = Propylene oxide.
TEA = Triethylamine.

TEMPERED/GASSY SYSTEM (TYPE Ib)

Method:

1. Analytical equations allowing for a broad range of overpressure (see appendix for illustration).

NON-TEMPERED (TYPE II)

Method:

1. Size vent to accommodate the total maximum vapor and gas generation rates, $\dot{Q}_v$ and $\dot{Q}_g$ respectively (see illustration in appendix).
2. Direct scaling approach provides an alternative method which usually yields a smaller vent size than method (1) above. This is because early loss of reactant from the vessel due to two-phase flow may be an advantage for non-tempered systems. Since this loss is always more effective in the process vessel than in the test cell due to much higher superficial velocities, direct scale-up in the current apparatus using top venting is hence possible [7]. A vent size that allows safe venting of the test sample and empties its content completely can then be safely extrapolated to full size based on area-to-charge scaling. Often a number of tests may be required to narrow in on the size that limits the pressurization to just below the allowable level.

SUMMARY OF TESTING RESULTS

Table 1 summarizes the testing results for some fifty-five chemical systems with both the self-heat rate at set condition and the required vent area per 1000 kg charge listed. Nearly all of these systems are operated in batch and semi-batch mode. Most however, have relief set pressures below 100 psig with the following distribution:

Set Pressure	Percent
0-20 psig	32
20-40 psig	36
> 40 psig	32

About seventy percent of these systems can be classified as tempered reactions. Among these, the most energetic ones were bulk polymerization of vinyl acetate and acrylate monomer mix, which exhibited self-heat rates as high

as 1000°C/min and 2000°C/min, respectively. Non-tempered systems generally exhibit high self-heat rates at venting simply because these rates normally would coincide with their peak rates just prior to complete consumption of the reactants. In some of these cases, the reactions were considered too energetic to be vented safely in a practical manner.

In general, the reactant concentration directly influences the self-heat rate at relief via (a) typical kinetic consideration where the reaction rate is proportional to the reactant concentration to the nth (order of reaction) power, (b) the dilution effect of the solvent (if present) which provides moderation of self-heat rate due to increase in heat capacity[1], and (c) alteration of the temperature at set condition simply from VLE consideration. The last item would be detrimental to those cases where a more volatile solvent is normally employed in the refluxing mode, thus the loss of the solvent in a mischarge incident (i.e., pure reactant instead) would not only result in faster reaction rate, but a higher energy release as a result of higher temperature at the relief set pressure. Hence, many examples of solvent mischarge as listed in Table 1 result in substantial increase in vent sizes above the normal reacting batch (e.g., Systems 3, 13, 14).

COMPARISON WITH FIA CHART[2]

The FIA chart [8, 9] makes specific vent sizing recommendations for various reaction categories because of the standardized nature of batch reactors (at least at the time it was done). The reacting systems of Table 1 which belong to these categories are therefore listed in Table 2 together with a few similar systems which had been characterized during earlier DIERS work [10]. The vent sizing recommendations based on current methodology with two-phase flow in relief devices are compared with FIA chart recommendations. This comparison is also illustrated graphically in Figure 1. Only pure styrene and pure methyl methacrylate systems under thermal initiation[3] are found to show agreement with FIA chart; the re-

[1]If a liquid specific heat is about the same for reactant and solvent, then this effect is redundant (i.e., same as Item 1) for a first-order reaction.

[2]It is noted that this chart has been withdrawn as an official document by Industrial Risk Insurers.

[3]Though 0.1% benzoyl peroxide was used in methyl methacrylate, the reaction was mainly thermal initiated polymerization.
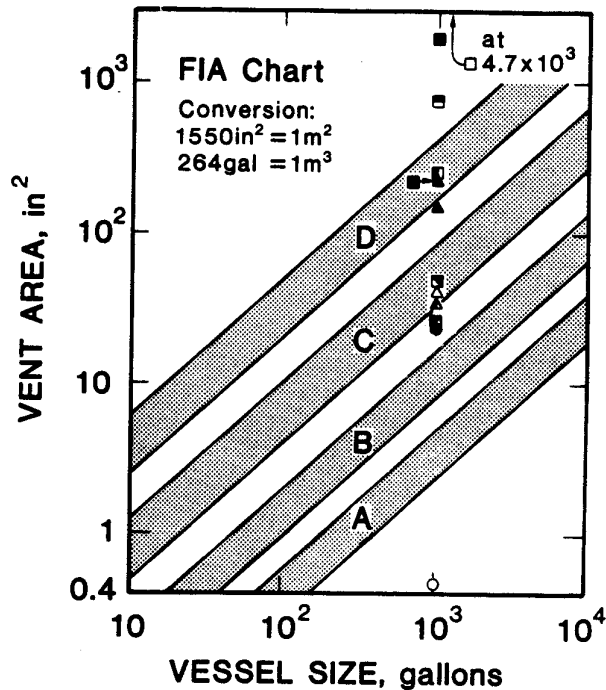

Figure 1. FIA chart recommendations versus current DIERS methodology.

maining systems exhibit varying degrees of discrepancies. For example, the presence of peroxide initiator in dilute styrene system resulted in nearly two orders of magnitude increase in self-heat rate (or energy release) at relief and hence in vent size. FIA chart underpredicts this case with initiator present. Similarly, vent sizes for both concentrated methyl methacrylate and ethyl acrylate systems with initiators were underpredicted by the chart.

Finally, the phenol-formaldehyde reaction with a caustic catalyst offers a good example of illustrating the inadequacy of the empirical FIA chart approach. Table 2 lists the wide range of self-heat rates observed at set condition depending on the particular recipe, and in most of these cases the recommendations based on the chart are nonconservative. Note also that the use of 37.5% formalde-

TABLE 2. COMPARISON OF PRESENT VENT SIZING METHODOLOGY WITH FIA CHART RECOMMENDATION
VESSEL SIZE: 1000 GALLONS

System	Reference	P_S psig	$(dT/dt)_s$ °C/min	Recommended Vent Area (m²)			
				This Study	FIA Chart	FIA Line	Symbol
35% Styrene in ethylbenzene (no initiator)	_(a)	30	0.3	2.9×10^{-4}	5.2×10^{-3}-0.011	B	O
<35% Styrene in solvent (with BPO initiator)	Table 1 (5)	30	12	0.015	5.2×10^{-3}-0.011	B	●
Pure styrene (no initiator)	DIERS Report	58	40	0.026	0.021-0.055	C	△
Pure methyl methacrylate (0.1% BPO)	DIERS Report	19	12	0.022	0.021-0.055	C	▲
Methyl methacrylate mix (with AIBN initiator)	Table 1 (13)	25	110-170	0.105-0.15	0.021-0.055	C	▲
Ethyl acrylate mix (with BPO initiator) Phenol-HCHO-Caustic:	Table 1 (14)	15	2000	3.1	0.11-0.28	D	□
Recipe I 37.5% HCHO	DIERS Report	15	7.5	0.017	0.11-0.28	D	◪
Recipe II 37.5% HCHO	Table 1 (4)	15[b]	14	0.031	0.11-0.28	D	◩
Recipe III 50% HCHO	Table 1 (1)	15	70	0.16	0.11-0.28	D	◨
Recipe IV 50% HCHO	Table 1 (2)	5	150	0.48	0.11-0.28	D	◧
Recipe V 50% HCHO	Table 1 (3)	15	50-500[c]	0.15-1.3	0.11-0.28	D	■

[a]Based on Hui-Hamielec kinetic model, Ref. [12].
[b]Use 15 psig instead of 100 psig.
[c]Double charge of caustic. (_) = System number in Table 1.

hyde solution leads to an order of magnitude lower rate than the use of 50% solution, while the accidental double charge of caustic resulted in a ten-fold increase in energy release (see Table 2, Recipe V). This comparison clearly illustrates that such a generalization of reaction categories in vent sizing application, as is done in the FIA chart, is inadequate and misleading. Instead thermal runaway data (self-heat rate and pressure rate) should be obtained using a representative sample[4] before a realistic assessment of emergency relief requirement can be made.

CONCLUSIONS

The new bench-scale apparatus and associated vent sizing methodology has been extensively tested for a wide range of chemical systems under runaway conditions. The methodology allows direct and safe extrapolation to field vessels at relatively low cost.

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APPENDIX
Illustrations of Vent Sizing Equations for Various Systems

All illustrations below are carried out in U.S. customary units (i.e., psi, ft, lbm, °F or °R, and Btu). The relief vent area is given in terms of an ideal nozzle area with discharge coefficient of unity. The application to actual relief design and layout is beyond the scope of this paper. The vent sizing methodology will be conservatively based on homogeneous-vessel (two-phase) venting, thus assuming negligible vapor/liquid separation within the vessel.

Case A: Phenol-Formaldehyde Example (Type Ia)

See Figure 10 of Ref. [2] for actual data.
P_s = 15 psig = 29.7 psia
V = 1200 gal. = 160 ft³
m_o = 8000 lbm
C_p = 0.7 Btu/lbm°F
P-T relation can be fitted by the Antoine equation
$P(psia) = \exp[a - b/T] = \exp[15.78 - 8798/T]$
where T is in °R
$T_s = 250.2°F = 710.2°R$
$(dT/dt)_s = 13.6°F/min.$
The two-phase discharge flow rate per unit area is evaluated according to the homogeneous equilibrium model and in the low quality region it can be approximated by [4, 5]

$$G = 0.9 (144) \frac{dP}{dT} \left(\frac{32.2}{778.16} \cdot \frac{T}{C_p} \right)^{1/2}$$

By noting dP/dT can be more conveniently replaced by bP/T²,

$$G = (0.9) (144) \frac{(8798)(29.7)}{(710.2)^2} \left[\frac{32.2}{778.16} \cdot \frac{710.2}{0.7} \right]^{1/2}$$

$$= 435 \text{ lbm/s.ft}^2$$

The analytical vent sizing equation for homogeneous vessel venting [4] is

$$A = \frac{m_o q}{G \left[\left(\frac{V}{m_o} \cdot \frac{144}{778.16} T \frac{dP}{dT} \right)^{1/2} + (C_p \Delta T)^{1/2} \right]^2}$$

For a 20% gage overpressure (OP),

$$T_m = 255.8°F = 715.8°R$$

$$\Delta T = T_m - T_s = 5.7°R$$

[4]This sample should take into consideration any credible upset condition such as mischarges of solvent and catalyst.

$$(dT/dt)_m = 15.1°F/min$$

$$q = \frac{1}{2} C_p \left[\left(\frac{dT}{dt} \right)_s + \left(\frac{dT}{dt} \right)_m \right] = 0.168 \text{ Btu/s.lbm}$$

Thus the required vent area for 20% OP

$$A_{20} = \frac{(8000) (0.168)}{435 \left[\left(\frac{160}{8000} \cdot \frac{144}{778.16} \cdot \frac{8798}{710.2} \cdot 29.7 \right)^{1/2} + (0.7 \cdot 5.7)^{1/2} \right]^2}$$

$$= 0.308 \text{ ft}^2 = \underline{44 \text{ in}^2}$$

As for comparison, the nomogram method [3][5] yields a vent area of 0.0077 m²/1000 kg charge for a (dT/dt)_s of 7.6°C/min (from 13.6°F/min). The actual vent required is therefore,

$$A = 8000 \text{ lbm} \frac{0.4536 \text{ kg}}{1 \text{ lbm}} \cdot \frac{0.0077 \text{ m}^2}{1000 \text{ kg}} \cdot \frac{1550 \text{ in}^2}{1 \text{ m}^2}$$

$$= \underline{43 \text{ in}^2}$$

which according to the nomogram is applicable to 20% absolute overpressure, or 40% gage overpressure. The nomogram yields slightly more conservative results.

Case B: Hydrogen Peroxide (50% wt) Example (Type Ib)

See Ref. [11] for actual data. The readers should be cautioned that this is only a hypothetical example as the data were taken in non-prototypic conditions. In a Type Ib system, an open vented test was conducted to obtain volumetric gas/vapor generation rate, partial pressure information and tempering temperature at the relief set pressure. The following parameters were obtained from the test:

m_t = 0.154 lbm
C_p = 0.8 Btu/lbm°F
V_c = 4 l = 0.141 ft³ (5 l was mistakenly used in Ref. [11])
P_s = 0.3 psig = 15.0 psia
T_s = 226°F = 686°R (tempering point)
dP/dt = 0.04 psi/s
dT/dt = 0.1°F/s

The above two rates were measured with the containment vessel sealed after attaining tempering. Hence the change in total pressure with respect to temperature can be approximated by

$$\Delta P/\Delta T = \frac{dp}{dt} \Big/ \frac{dT}{dt} = 0.4 \text{ psi/°R} = 57 \text{ lb}_f/\text{ft}^2°R$$

This value, however, is higher than the theoretical value of about 40 lb_f/ft²°R [13]. It might be more appropriate instead to use two tempering points (one at a higher back pressure of say a few psi) to evaluate $\Delta P/\Delta T$, thus overcoming the difficulty of measuring small pressure and temperature increments. At the end of the dP/dt and dT/dt measurement period, the adiabatic temperature rise was determined by raising the containment pressure quickly. Here

$$(dT/dt)_a = 0.79°F/s \text{ (0.1°F/s is due to external heating)}$$

The vapor volumetric generation rate is then

$$\dot{Q}_v = \frac{778.16 \, m_t C_p \left(\frac{dT}{dt} \right)_a}{144 \, T \left(\frac{\Delta P}{\Delta T} \right)}$$

$$= 2.0 \times 10^{-3} \text{ ft}^3/\text{s per test sample}$$

If the volatile component is known, it is advisable to check the above rate by replacing T $(\Delta P/\Delta T)$ with $\rho_v \lambda$ (vapor density × latent heat of vaporization). Based on water property, $\dot{Q}_v$ is estimated to be 2.7×10^{-3} ft³/s instead.

[5]The nomogram method is based on an assumed temperature of 720°R (400 K) and a C_p value of 0.6 Btu/lbm°R. Its equation form can be given by

A = 2.08×10^{-3} dT/dt (°C/min)/P_s(bar), m²/1000 kg
= 11.8 dT/dt (°F/min)/P_s(psia), in²/1000 lb.

The gas (oxygen) volumetric generation rate is given by

$$\dot{Q}_g = \frac{V_c}{P_s}\left(\frac{T_s}{T_c}\right)\frac{dP}{dt}$$

$$= 4.8 \times 10^{-4}\ ft^3/s\ \text{per test sample}$$

Here (T_s/T_c) is the temperature correction according to ideal gas law and is taken to be (686/545).

It can be shown that at the tempering condition, the partial pressures and the volumetric rates are related via

$$\frac{p_v}{p_g} = \frac{\dot{Q}_v}{\dot{Q}_g}$$

Thus

$$p_v = P_s\frac{\dot{Q}_v}{\dot{Q}_v + \dot{Q}_g} = 12.0\ psi$$
$$p_g = P_s - p_v = 2.9\ psi$$

Theoretical values should be 12.4 psi and 2.6 psi respectively [13]. Now, the particular vessel and charge are defined

V	$= 58.8\ ft^3$
m_0	$= 2205\ lbm$
α_0	$= 0.5\ \text{(free-board volume fraction)}$
$\dot{Q}_g$	$= 6.87\ ft^3/s$
$\dot{Q}_v$	$= 28.6\ ft^3/s$

We proceed first to evaluate the two-phase mass discharge rate per unit area. The following formula is recommended.

$$G \doteq \frac{p_v}{P}G_v + \left(1 - \frac{p_v}{P}\right)G_g$$

where

$$G_v = (0.9)(144)\frac{dp_v}{dT}\left(\frac{32.2}{778.16}\cdot\frac{T}{C_p}\right)^{1/2}$$

and

$$G_g \doteq [2(144)(32.2)\left(\frac{m_0}{V}\right)(P - P_{amb})]^{1/2}$$

Thus G_v is the low-quality homogeneous equilibrium flashing flow approximation and P is the average system pressure during venting. Here G_g is the nearly incompressible Bernoulli flow approximation. Consider the case of 4.7 psi overpressure, P will hence be (15.0 + 19.7)/2 or 17.4 psia and the available pressure drop $(P - P_{amb})$ is therefore 2.65 psi. If significant pressure drop is encountered, the G_g evaluation should be based on the compressible model as outlined in Part C. The above expressions give 247 lbm/s.ft² and 960 lbm/s.ft² respectively for G_v and G_g. Finally, the two-phase mass discharge rate per unit area is

$$G \doteq \frac{12.0}{17.4}(247) + \left(1 - \frac{12.0}{17.4}\right)(960)$$

$$= 470\ lbm/s.ft^2$$

Note that the augmentation is still significant when compared with the flashing flow component which is about 250 lbm/s.ft² in this case. The analytical equation employed in Case A example can be applied in the present case but ΔT should be conservatively evaluated based on closed-system consideration. This can be estimated as follows:

$$\left(\frac{\Delta P}{\Delta T}\right)_{closed} = \frac{dp_v}{dt} + \frac{dp_g}{dt}\bigg/\frac{dT}{dT}$$

$$= \frac{p_v}{P_s}\frac{dP}{dT} + \frac{P_s\dot{Q}_g}{\alpha_0 V}\bigg/\frac{dT}{dt}$$

$$= \left(\frac{12.0}{15.0}\right)(0.4) + \left(\frac{15.0\cdot6.87}{0.5\cdot58.8}\right)\bigg/0.79$$

$$= 0.32 + 4.44$$

$$= 4.8\ psi/°F$$

Note that the second term, i.e., the gas accumulation term, dominates. To calculate the corresponding available temperature rise, we write

$$\Delta T = \frac{\Delta P}{(\Delta P/\Delta T)_{closed}} = \frac{4.7}{4.8} = 0.98°F$$

Though this value may appear small, the product $C_p\Delta T$ is about the same order of magnitude as the latent heat of cooling term.

The average energy release is given by

$$q = \frac{1}{2}C_p\left[\left(\frac{dT}{dt}\right)_s + \left(\frac{dT}{dt}\right)_m\right]$$

$$\doteq C_p\left(\frac{dT}{dt}\right)_s = 0.6\ Btu/s.lbm$$

Finally, the vent sizing equation can be similarly written as

$$A = \frac{m_0\ q}{G\left[\left(\frac{V}{m_0}\cdot\frac{144}{778.16}T\frac{dp_v}{dT}\right)^{1/2} + (C_p\Delta T)^{1/2}\right]^2}$$

$$= \frac{(2205)(0.6)}{470\left[\left(\frac{58.8}{2205}\cdot\frac{144}{778.16}686\cdot0.32\right)^{1/2} + (0.8\cdot0.98)^{1/2}\right]^2}$$

$$= \frac{(2205)(0.6)}{470[1.04 + 0.88]^2} = 0.76\ ft^2 = \underline{110\ in^2}$$

Case C: Non-Tempered Gassy Example (Type II)

The required vent area is sized to cope with the total *maximum* vapor and gas generation rates, $\dot{Q}_{tot} = \dot{Q}_v + \dot{Q}_g$;

$$A = \frac{\dot{Q}_{tot}}{Gv}$$

Typically for these systems, $\dot{Q}_g >> \dot{Q}_v$ and $\dot{Q}_t$ can be estimated from the maximum pressure rise rate $(dP/dt)_{max}$ in either closed-system or open-system tests. For a given allowable overpressure ΔP, the peak pressure is therefore $P_s + \Delta P$ (usually this peak pressure is chosen to be 1.1 times MAWP of the vessel). Assuming ideal gas behavior,

$$\dot{Q}_{tot} \doteq \frac{V_g}{(P_s + \Delta P)}\left(\frac{T_t}{T_c}\right)\left(\frac{dP}{dt}\right)_{max}\left(\frac{m_0}{m_t}\right)$$

The last term on the right side is the reacting mass scale-up factor. Here (T_t/T_c) is the temperature correction due to cooler containment atmosphere. If closed system test data are used, this correction term becomes unity. Here the available gas volume is denoted by V_g.

At low free-board volume fraction, say $\alpha_0 < 0.05$, the discharge flow can be approximated by the incompressible Bernoulli equation.

$$Gv = \sqrt{2v(P_s + \Delta P - P_{amb})(144)(32.2)}$$

where v is the average specific volume given by V/m_0.

A more widely applicable model would resort to the nonflashing (frozen) two-phase critical flow model [14] which in the limit of isothermal flow (i.e., thermal equilibrium or vapor specific heat ratio of unity; this assumption yields conservative results) can be approximated by the following equations for critical pressure ratio η and G_v,

$$\eta = \left[2.016 + \left(\frac{1 - \alpha_0}{2\ \alpha_0}\right)^{0.7}\right]^{-0.714}$$

$$Gv = \sqrt{(P_s + \Delta P)v(144)(32.2)}\ G^*$$

where

$$G^* = \frac{\left\{\frac{2}{\alpha_0}\left[\left(\frac{1 - \alpha_0}{\alpha_0}\right)(1 - \eta) - \ln\eta\right]\right\}^{1/2}}{\frac{1}{\eta} + \left(\frac{1 - \alpha_0}{\alpha_0}\right)}$$

Here subcritical (subsonic) flow would be indicated by $P_{amb} > \eta(P_s + \Delta P)$ and if this inequality holds, then η is given by $P_{amb}/(P_s + \Delta P)$ and is to be used in the subsequent evaluation of Gv.

A hypothetical example is illustrated below.

P_s = 25 psig = 39.7 psia
V = 750 gal = 100 ft^3
α_0 = 0.04
m_0 = 6000 lbm
m_t = 0.22 lbm
$(dP/dt)_{max}$ = 1.1 psi/min = 0.018 psi/s
T_t = 482°F = 942°R
T_c = 104°F = 564°R
V_g = 0.141 ft^3
P_{amb} = 14.7 psia

For a given overpressure of 10%,

ΔP = 2.5 psi

$$Q_{tot} = \frac{(0.141)}{(39.7 + 2.5)} \frac{(942)}{(564)} (0.018) \left(\frac{6000}{0.22} \right)$$

$$= 2.74 \text{ ft}^3/\text{s}$$

$$G_v = \left[2\frac{(100)}{6000} (39.5 + 2.5 - 14.7) (144) (32.2) \right]^{0.5}$$

$$= 65 \text{ ft/s}$$

$$A = \frac{2.74}{65} = 0.042 \text{ ft}^2 = \underline{6.0 \text{ in}^2}$$

Using the more exact nonflashing two-phase flow model yields a Gv value of 61.4 ft/s and a vent area of 6.4 in². This latter method is recommended for $\alpha_0 > 0.05$.

Symbols Used In Appendix

A = vent area
C_p = liquid-phase specific heat
G = discharge mass flow rate per unit area
m_0 = reactor charge
m = mass
P = pressure
p = partial pressure
q = energy release rate
$\dot{Q}$ = volumetric generation rate
T = temperature
V = reactor vessel volume
V_g = free-board gas volume
v = specific volume
α_0 = initial free-board volume fraction
η = critical pressure ratio
ϕ = phi-factor or thermal inertia
λ = latent heat of vaporization
ρ = density

Subscripts

a = adiabatic
amb = ambient
c = containment
g = noncondensable gas
l = liquid
m = pressure turnaround
o = initial
s = relief set condition
t = test sample
tot = total
v = vapor

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