THE REACTIVE SYSTEM SCREENING TOOL (RSST): AN INEXPENSIVE AND PRACTICAL APPROACH TO SIZING EMERGENCY RELIEF SYSTEMS

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SUMMARY

An inexpensive practical approach to sizing venting requirements for reactive chemical systems is outlined. Based upon easy to obtain RSST data, the approach provides a consistent comparison with all available large-scale data including vapor, hybrid and gassy reactions.

1. INTRODUCTION

Knowledge of chemical reaction rates, character, and energy release is essential to modern process design. The Design Institute for Emergency Relief Systems (DIERS) program (Fisher, 1985), sponsored by 29 companies under the auspices of the AIChE and completed in 1985, provided the chemical process industry with tools necessary to gather such data (Fauske & Leung, 1985). A primary purpose of the effort was evaluation of emergency relief vent requirements, including energy and gas release rates for systems under upset conditions and the effects of two-phase flow on the emergency discharge process. An easy, inexpensive approach to the DIERS procedure was later provided by the RSST (Creed and Fauske, 1990 and Fauske, 1993). This paper provides an update of the RSST methodology with emphasis on benchmarking the methodology against all available large-scale data including vapor, hybrid, and gassy reactive systems.

2. RSST DESCRIPTION

The RSST (Figures 1 and 2) consists of a spherical glass reaction vessel and immersion heater (optional), its surrounding jacket heater and insulation, thermocouples and a pressure transducer, a stainless steel containment vessel that serves as both a pressure simulator and safety vessel, and, not shown, a magnetic stirrer base, a control box containing the heater power supply, temperature amplifiers, and a data acquisition and control panel. The sample cell volume is 10 ml and the containment volume is 350 ml. A key feature of the apparatus is its low effective heat capacity relative to that of the sample whose value, expressed as the capacity ratio, is approximately 1.04 (i.e., quite adiabatic). This feature allows the measured data to be directly applied to process scale.
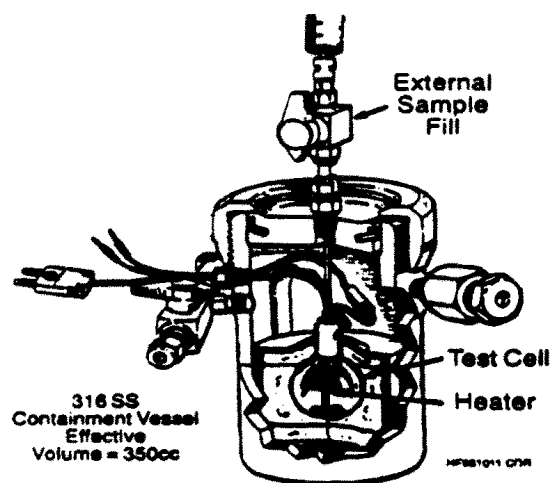

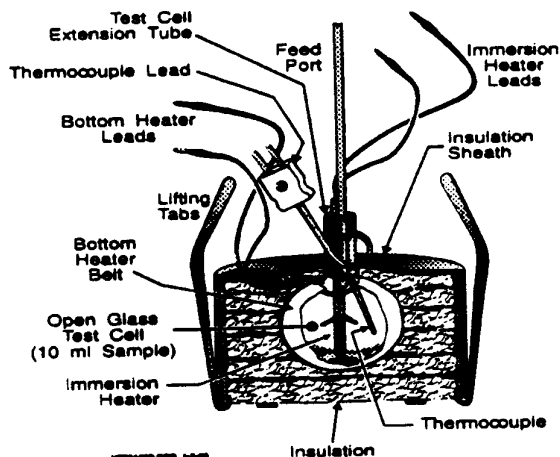**Figure 1. Reactive System Screening Tool (RSST) containment.**

Figure 2. Reactive System Screening Tool (RSST) test cell.

Typically, a 10 mλ sample is heated at a constant rate and the sample self-heat rate is found as a function of sample temperature. The imposed linear ramp rate can be varied from 0.1°C/min. to ramp rates approaching those required to simulate fire exposure by using the immersion heater option. The heater compensates for losses, and the self-heating rate of an exothermic system is adjusted for heater input. Reagents may be added to a sample during a test. Data handling programs produce plots of pressure vs. temperature, temperature vs. time, pressure vs. time, and Arrhenius plots.

The RSST quickly and safely determines the potential for runaway reactions and measures the rates of temperature and, in case of gassy reactions, pressure increases to allow reliable determinations of the energy and gas release rates. A recent additional feature of the RSST allows flow regime characterization, i.e., "foamy" versus "non-foamy" behavior, to be determined under actual runaway conditions (Fauske, 1998). This information can be combined with analytical tools (summarized later) to assess reactor vent size requirements.

3. SYSTEM CHARACTERIZATION AND VENT SIZING

Three types of reactive systems are distinguished for their venting and mitigation character (see Figure 3). A vaporizing, or tempered system contains components (often a solvent) whose vapor-liquid equilibrium controls the system temperature and reaction rate for a fixed containment pressure. This occurs when one or more components boil prior to potential gaseous decomposition, so heat from exothermic reactions is removed by the latent heat of vaporization, and the system pressure is equal to the component vapor pressure. In the RSST, one compound (or

more) evaporates from the glass vessel and condenses on the cold containment walls, thereby removing the reaction energy and tempering the system, as would occur in a vented reactor. So long as there is sufficient tempering liquid before the reactants are exhausted, and the vent is sized to pass the vapor as it is produced, tempering will limit the pressure rise. The principal parameter determining the vent size is the rate of temperature at the relief set pressure.
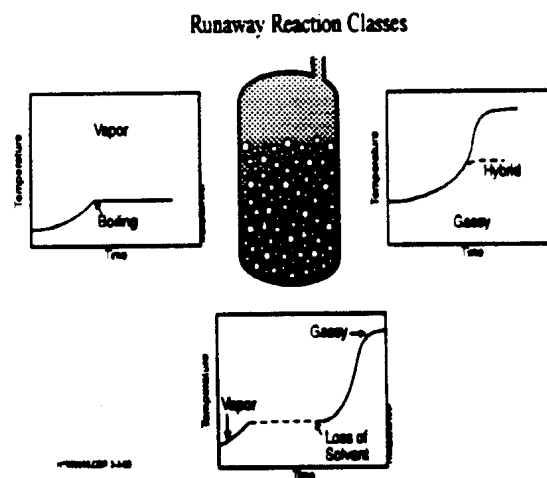

Figure 3. Illustration of vapor, hybrid and gassy reactive systems.

A gassy system has noncondensable reaction or decomposition products which continually increase the containment pressure and do not effectively temper the system, whose temperature may escalate rapidly. The total pressure is equal to the gas pressure, and the maximum rate of pressure rise determines the vent size. Note that a vapor system may evolve into a gassy one when tempering is lost by complete boiloff of solvent.

A hybrid exhibits both tempering and gassy characteristics. Gaseous decomposition occurs prior to boiling, but the rate of reaction (gas production by decomposition) is still tempered by vaporization. The total pressure in the reactor is the sum of the gas partial pressure and the vapor pressure, and both the rates of temperature and pressure rise are needed to determine the proper vent size.

3.1 Vapor System Sizing

The principal quantity of interest is the reaction self heat rate, $\hat{T}_s$ (K s^{-1}) at the relief set pressure, P_s (Pa) and temperature, T_2 (K). The $\hat{T}_s$ value is provided by the RSST and can be applied directly to

assess the vapor volumetric generation rate, $\dot{Q}_v$ (m^3 s^{-1}) from

$$\dot{Q}_v = \frac{m\, c\, \dot{T}}{\lambda\, \rho_v} \qquad (1)$$

where m (kg) is the reactant mass, c (J kg^{-1} K^{-1}) is the specific heat, λ (J kg^{-1}) is the latent heat of vaporization and ρ_v (kg m^{-3}) is the vapor density. Considering vapor venting only, the required vent area, A_v (M^2) can be estimated from

$$A_v \approx \frac{3}{2}\frac{m\, c\, \dot{T}}{C_D\, \lambda\, P_s}\left[\frac{R\, T_s}{M_{w,v}}\right]^{1/2} \qquad (2)$$

$$A_v \approx \frac{m\, c\, \dot{T}}{C_D\, P_s\left[2\left(1 - P_b / P\right)^{1/2}\right]}\left[\frac{R\, T_s}{M_{w,v}}\right]^{1/2} \qquad (3)$$

for critical and highly subcritical flow conditions, respectively, where C_D is the discharge coefficient, P_b (Pa) is the back pressure, R (8314 Pa-m^3/K-kg-mole) is the gas constant, and $M_{w,v}$ is the molecular weight.

Vent areas from available large-scale experiments with "non-foamy" or "churn turbulent" like systems (10 m^3 methanol/acetic anhydride, Linga et al., 1998, and 2 m^3 high conversion (HC) ethylbenzene/styrene, Fisher, et al., 1992) are compared to values from Equation 2 in Figure 4. The solid lines through the normalized data illustrate the well-known "overpressure" effect in reducing the vent area when two-phase flow is occurring (Leung, 1987 and Fauske, 1989). In fact, both theory and the data show that for "non-foamy" systems and allowance of modest "overpressure", the required vent area can be assessed considering vapor venting only, i.e., Equation 2.
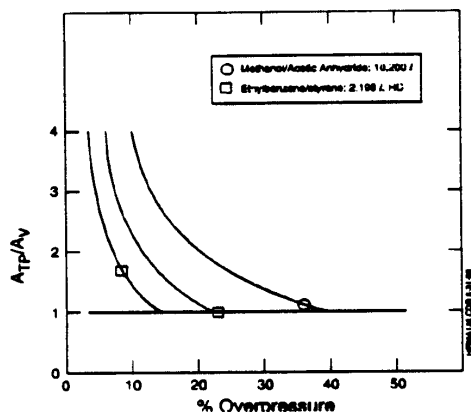

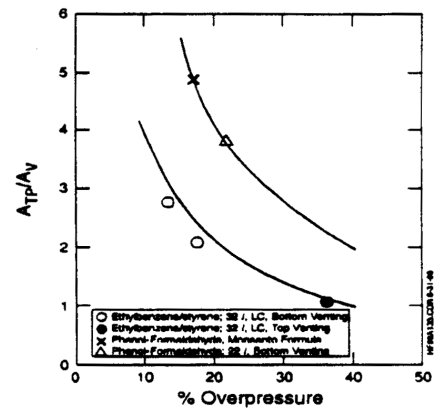Figure 4. Illustration of "non-foamy" experimental data (A_{TP}) and comparison with all vapor venting (A_v).

Figure 5. Illustration of "foamy" or "bubbly-like" experimental data (A_{TP}) and comparison with all vapor venting (A_v).

The vent sizing formula, A (in^2) = 0.053 V (gal), based upon large-scale experience and used for phenol-formaldehyde reactors (Howard, 1973), is used to illustrate the "overpressure" effect on venting requirements in Figure 5 for "foamy" or "bubbly-like" systems. Noting that the Monsanto formula is based upon a P_s value of 1-2 psig and a $\dot{T}_s$ value of about 6.5ºC min^{-1}, we estimate that the formula represents an "overpressure" of about 17%. At this overpressure the value of A_{TP}/A_v is about 4.9[*] (see Figure 5). The noted overpressure of 17% and the solid curve representing the "overpressure" effect are obtained by combining the Monsanto formula with the homogeneous vessel and vent flow formula $A_{TP} = (m\,\dot{T})/2\,(T_s/c)^{1/2}\,\Delta P$, where ΔP (Pa) is the overpressure (Fauske, 1989). The latter formula is in good agreement with the low conversion (LC) ethylbenzene/styrene data (Fisher et al., 1992) exhibiting "bubbly-like" behavior (see Figure 5). The interpretation of the Monsanto formula is also in excellent agreement with recent 22λ bottom vented phenol-formaldehyde tests (Leung et al., 1998). For a measured overpressure of 21.7% the value of A_{TP}/A_v is about 3.8 (see Figure 5).

Considering the enveloping nature of the phenol-formaldehyde system with its water-like properties, both theory and large-scale experience suggest that for "foamy" systems and allowance of modest "overpressure", an adequate vent size can be based upon large-scale fire exposure experiments with "foamy" and "non-foamy" water systems (Fauske, 1986).

3.2 Hybrid System Vent Sizing

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[*] It is of interest to note that for a P_s value of 1-2 psig and zero overpressure, this ratio would be about 160 based upon flashing two-phase flow condition.

The unique design offered by the RSST is ideally suited to characterize vent requirements for hybrid systems. The measured self heat rate, $\dot{T}$ ($K\ s^{-1}$), and rate of pressure rise, $\dot{P}$ ($Pa\ s^{-1}$), for a given relief set pressure, P_s (Pa), can be applied directly to assess the total gas-vapor volumetric rate, $\dot{Q}_T$ ($m^3\ s^{-1}$)

$$\dot{Q}_T = \dot{Q}_v + \dot{Q}_g = \frac{m\,c\,\dot{T}}{\lambda\,\rho_v} + v\frac{\dot{P}}{P_s}\frac{m}{m_t} \qquad (4)$$

where v ($3.5 \bullet 10^{-4}\ m^3$) is the RSST containment volume and m_t (kg) is the RSST sample mass. Considering gas-vapor venting only, the vent area to volume ratio, A/V (m^{-1}) can be estimated from

$$\frac{A}{V} \approx \frac{3}{2C_D}\left[\frac{\rho\,c\,\dot{T}}{\rho_v\,\lambda} + \frac{\rho\,v\,\dot{P}}{m_t\,P_s}\right]\left[\frac{M_w}{R\,T_s}\right]^{1/2} \qquad (5)$$

$$\frac{A}{V} \approx \frac{1}{C_D}\left[\frac{\rho\,c\,\dot{T}}{\rho_v\,\lambda} + \frac{\rho\,v\,\dot{P}}{m_t\,P_s}\right]\left[\frac{M_w}{2\left(1\text{-}P_b/P_s\right)R\,T_s}\right]^{1/2} \qquad (6)$$

for critical and highly subcritical flow conditions, respectively, where ρ (kg/m^3) is the loading density.

The above vent sizing methodology for hybrid systems is consistent with the large-scale 200 kg 50 wt% H_2O_2 runaway reaction trials reported by Wilberforce (1988), as illustrated in Figure 6. The absence of two-phase flows as the tempering is approached for these test trials is another example of the flow regime complexity during runaway reaction conditions. Apparently in these trials the vapor-gas release is highly non-uniform due to inherent non-equilibrium conditions with the majority of the release occurring at the free liquid surface, resulting in insignificant liquid swell in the absence of "foamy" conditions (Fauske et al., 1986).

Considering the often used DIERS two-phase flow methodology of "churn-turbulent" flow regime with C_o = 1.5 (Fisher et al., 1992), a self-heat rate at tempering in excess of 3.4°C min^{-1} would result in liquid ejection or two-phase flow, which is clearly not the case. However, we note that consistent with the above discussion for vapor systems, a vent area based upon all gas-vapor venting for a self heat rate
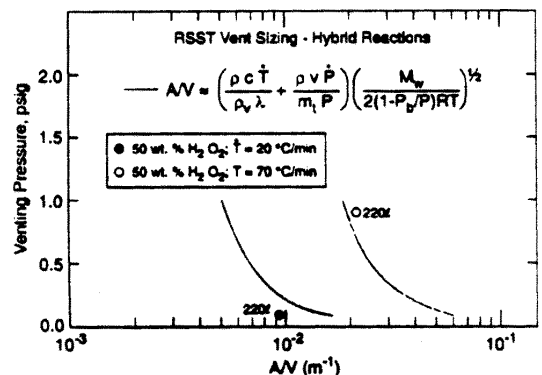

Figure 6. Comparison of H_2O_2 decomposition data with prediction from the RSST venting formula.

at tempering of 70°C min^{-1}, would only result in about 30% overpressure (~ 4.4 psi) in case of exercising the DIERS methodology. The lesson learned here, is that allowance for a modest overpressure eliminates the need to consider uncertainties related to flow regimes and non-equilibrium effects.

3.3 Gassy System Vent Sizing

For these systems Equation 5 reduces to

$$\frac{A}{V} \approx \frac{3}{2C_D}\frac{\rho\,v\,\dot{P}}{m_t\,P}\left(\frac{M_w}{R\,T}\right)^{1/2} \qquad (7)$$

and the maximum rate of pressure rise, $\dot{P}$, is of principal interest and again is provided by the RSST.

Available venting data for peroxide systems, 37.5 wt% 3,5,5 trimethyl hexanoyl peroxide (Wakker and deGroot, 1996), neat dicumyl peroxide (Gove, 1996), and t-butyl peroxy bensoate (Wakker and deGroot, 1996) are compared to predictions from Equation 7 in Figure 7, illustrating good agreement with both low, intermediate and high peroxide energetics levels. The RSST measured peak $\dot{P}$ values for these systems ($m_t \approx 0.01$ kg) are 1000, 4000 and 100,000 psi min^{-1} for 37.5 wt% 3,5,5 trimethyl hexanoyl peroxide, neat dicumyl peroxide and t-butyl peroxy benzoate, respectively. The predictions for neat dicumyl peroxide are also consistent with incident data reported by Gove (1996).
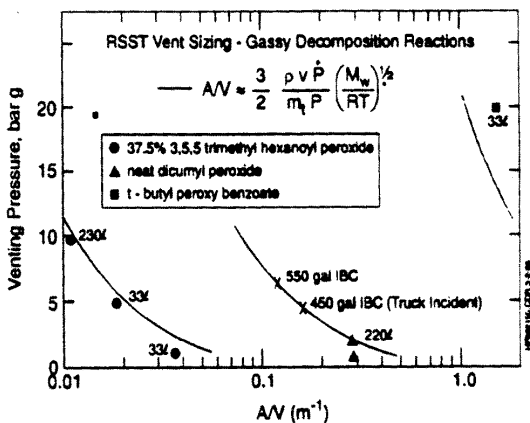
Figure 7. Large-scale runaway peroxide decomposition data and comparisons with RSST simulation with all gas venting.

We note that the DIERS' methodology for gassy systems considering initiation of two-phase flow at the measured peak reactive conditions and no prior material loss overestimate the vent areas noted in Figure 7 by at least an order of magnitude. As indicated by the RSST tests, significant material losses occur well before reaching peak reactive conditions, further justifying the assumption of gas venting only. Furthermore, it is of interest to note the transition from a homogeneous to propagating reaction behavior as the peroxide energetics level increases (Fauske, 1998a and Grolmes, 1998). Such transitions strongly influence the peak volumetric gas generation rate and require experimental determination as provided by the RSST. The transition, as well as the rage of propagation cannot be predicted by theoretical means.

SUMMARY

Due to its ease of use as well as its low cost, the RSST is now a standard industry tool for chemical system characterization for relief system design data acquisition. The RSST data which can be scaled directly to full-size applications have been demonstrated to produce excellent agreement with a large number of large-scale venting tests including vapor, hybrid and gassy systems. Easy to use design equations are provided for these systems.

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