

New Experimental Technique For Characterizing Runaway Chemical Reactions

The bench-scale apparatus provides the data that can be extrapolated directly to full-size process vessels for vent sizing: measurements of thermal data under nearly adiabatic conditions as well as flow regime and viscosity characterization under runaway conditions.

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Sizing of adequate emergency relief systems (ERS) to protect against runaway chemical reactions is often difficult, because there are not enough data on the chemical energy release rate and necessary thermophysical property of relief conditions. To help solve this problem, a bench-scale apparatus that meets the following requirements was developed:

- Handle largely unknown systems—energy release rates ranging from 0.1 to 10 W/g.
- A small test sample (~100 mL) to assure safe and easy handling.
- Direct extrapolation to large scale: safe but not overly conservative.
- Relatively inexpensive.

Feature of the equipment

The key feature of the equipment is the use of a unique low heat capacity test cell design to reduce the thermal mass. With a test cell volume of ~120 mL and a wall thickness of ~0.13 mm, an adiabaticity factor of ~1 is achieved. The test cell is enclosed in a larger pressure vessel with a pressure capability of about 2,000 psi (13.8 MPa), Figure 1. The weight of the stainless steel test cell including the Teflon-encapsulated magnetic stirrer is approximately 21 g yielding a ϕ factor of about 1.05.

The weakness of the test cell is compensated by either using a pressure equalization system such that the test cell sees only a slight pressure difference with its surroundings or by having the test cell open depending on the mode of operation. For closed system tests, the inner vessel and outer vessel pressures are measured by separate transducers. The large containment pressure vessel serves to prevent the bursting of the test cell by regulating the vessel pressure to follow the test cell pressure. By using appropriate solenoid valves, pressure changes [up to about 500 psi (3.4 MPa)/s] are rapidly equilibrated.

A heater coil is situated immediately outside the stainless steel test cell in an insulation assembly. Because it is not in direct contact with the cell, however, most of the energy is transferred to the cell wall via convective- and radiative-type heating. The sole purpose of this inner heater is to provide the necessary external power to heat the sample up to the temperature level where the exotherm can be detect-

ed. The outer guard heater coil is fastened onto the outside wall of the aluminum can and this can is separated from the test cell by a uniform layer (~4 mm thick) of fiberfrax insulation. A fast response thermocouple is attached to the inside surface of the can, and the temperature difference between the steel cell and the outer aluminum can is maintained to a minimum by supplying power to the guard heater. Thus, heat loss to the surroundings is kept to a minimum (1).

Test procedures

This bench-scale apparatus can be used to characterize runaway chemical reactions in closed as well as in open or vented systems. Information include thermal data (closed system), and flow regime and viscosity characterization (open system).

The low heat capacity closed test cell design along with elimination of significant heat losses is ideally suited for obtaining thermal runaway data. They include determination of the onset of thermal instability, temperature of no return and time to maximum rate. Here the principal measurements used are the temperature and pressure inside the test cell as a function of time. Both pressure and temperature equalization techniques are used. The former enables the test cell to maintain its integrity at elevated pressures and the latter enables the test cell to achieve essentially an adiabatic runaway condition.

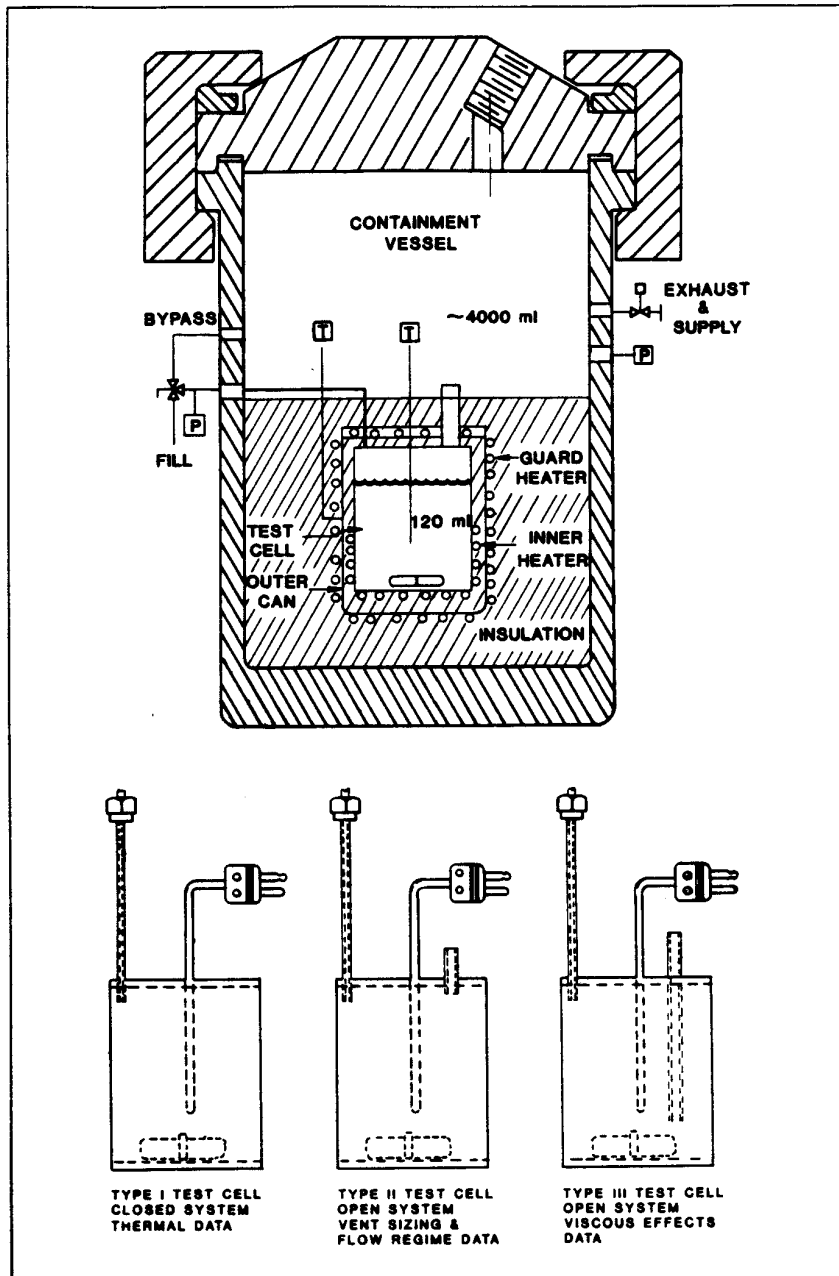
The following test procedures were used for acquiring thermal data (2).

1. The test cell can be loaded either outside the containment vessel or after it is placed inside the containment vessel by using the remote addition line. Pad gas can be eliminated before heating by simultaneously pulling a vacuum on the test cell and the containment vessel, again using the remote addition line.

2. A runaway reaction is initiated by supplying heat to the sample using the test cell heater in a stepwise fashion (heat-wait-search mode). At the onset of exotherm, the test cell heater is turned off and the guard heater is operated to assure negligible heat losses.

3. Pressure in the containment vessel is regulated to follow the test cell pressure.

Figure 1. Small-scale test equipment with closed and open test cell designs.



4. When reaction is completed, power is turned off to the guard heater, and the test sample is allowed to cool slowly.

Measured thermal runaway data for the 80% Styrene/20% ethylbenzene system are shown in Figures 2 through 5. The temperature history, Figure 2, is well predicted using Hamielec's kinetic model (3). The total pressure prediction, Figure 3, contains the correction due to the Flory-Huggins theory of polymer solution of styrene vapor pressure and the liquid thermal expansion effect on pad gas pressure. In

terms of the self-heat rate, Figure 4, excellent agreement with Hamielec's kinetic model is exhibited throughout the entire temperature range.

Flow regime

Discrimination between foamy and nonfoamy behavior is of special interest in assessing disposal requirements of vented material. For this purpose, the bench-scale equipment

Figure 2. Temperature data: Test CC-22 (80% styrene) vs. Hamielec's kinetic model predictions.

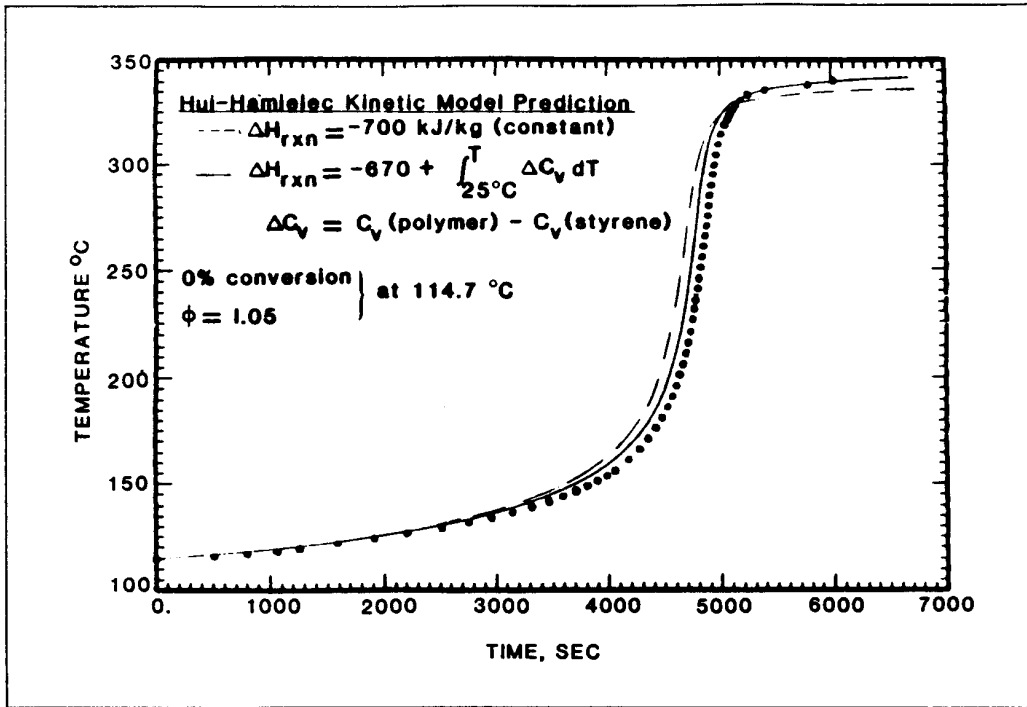


Figure 3. Pressure data: Test CC-22 (80% styrene) vs. Hamielec's kinetic model predictions (using temperature-dependent heat of reaction).

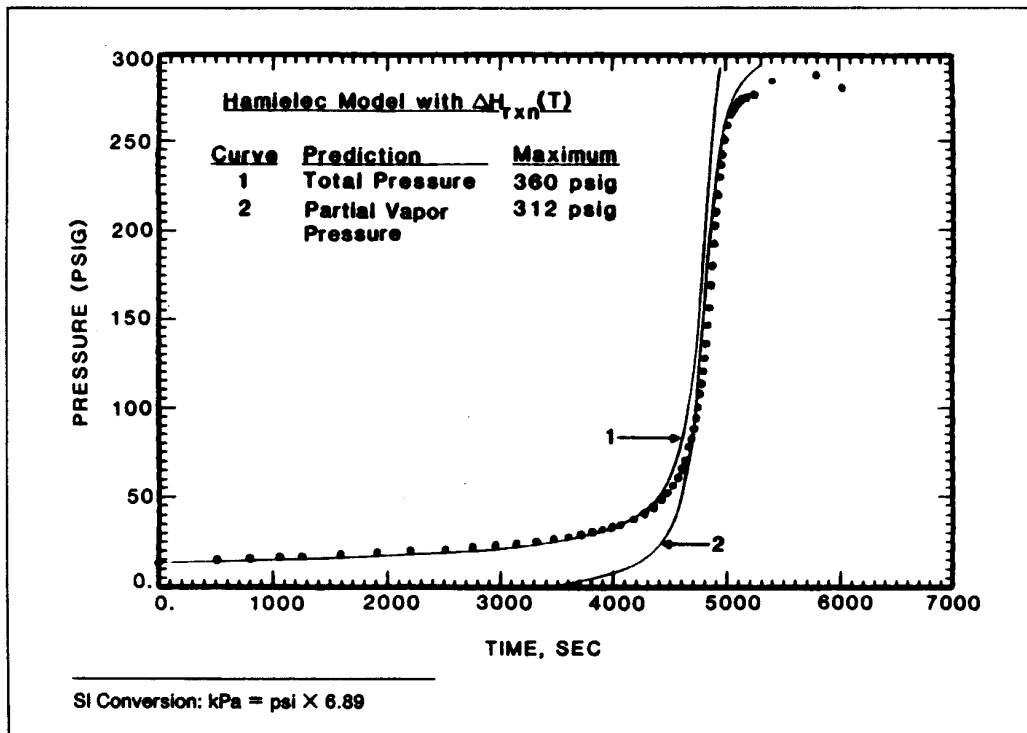


Figure 4. Self-heat rate data: Test CC-22 (80% styrene) vs. Hamielec's model.

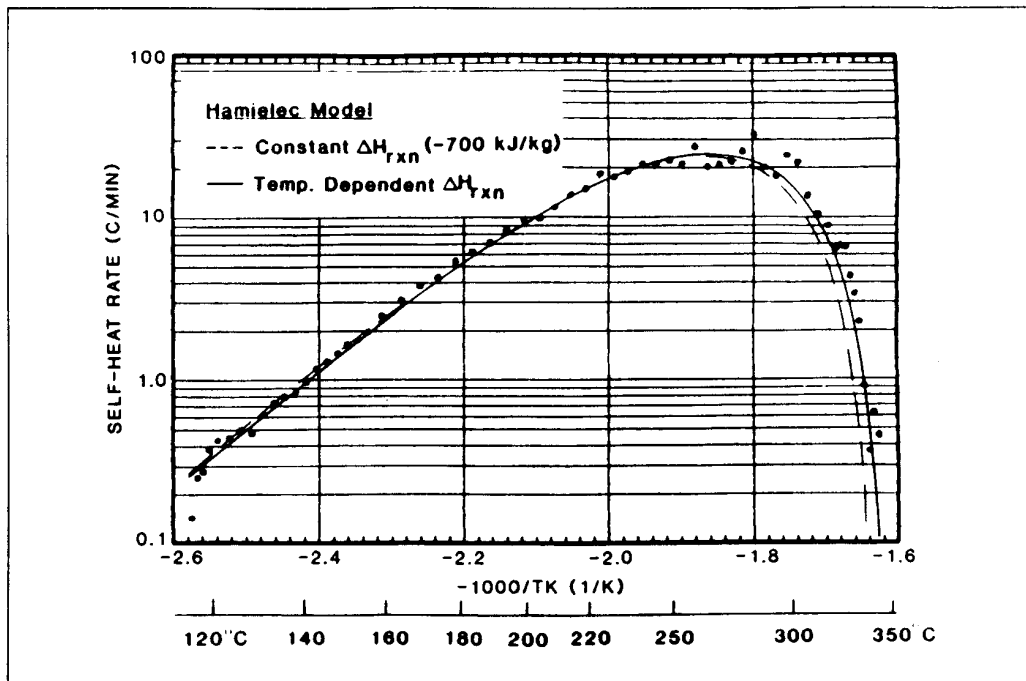


Figure 5. Typical depressurization characteristics of tempered systems.

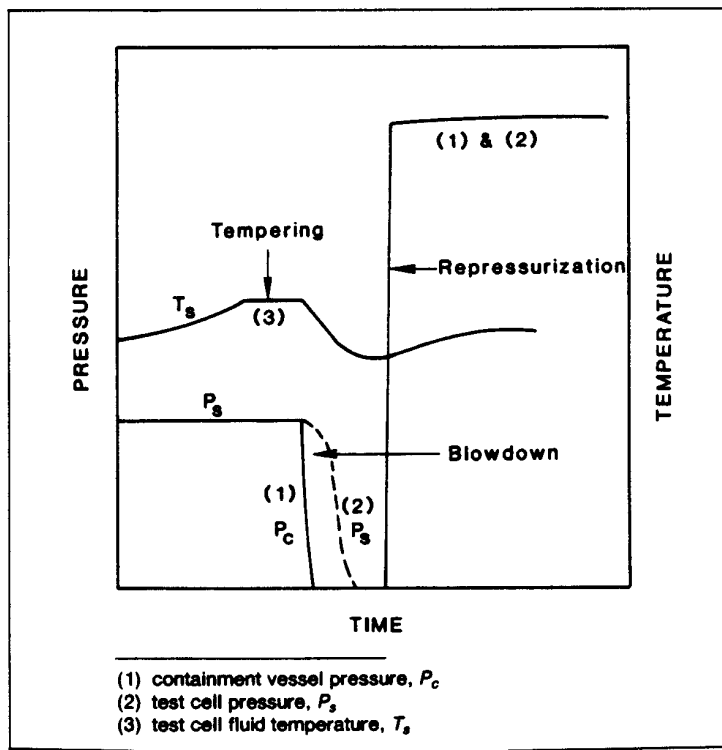


Table 1. Examples of flow regime data.

Test Fluid	Temp. Relief, °C	P_{sat} , kPa	Experimental*		Flow Regime Characterization
			α_o	α_s	
Water	152	500	0.13	0.53	Nonfoamy
Soapy Water (1,000 ppm Detergent)	152	500	0.11	0.98	Foamy
Styrene (Runaway)	219 (Tempered)	510	0.08	0.95	Foamy

* α_o = free-board volume fraction at relief
 α_s = free-board volume fraction at the end of blowdown

using a top vented test cell and the blowdown technique can be used to simulate a runaway reaction in a large process vessel. (The runaway reaction in a small test cell and at constant pressure by itself is very misleading since its superficial vapor velocities are very small compared to those in large process vessels.) Therefore, the typical range of superficial velocities can be simulated in the small test cell by choosing the proper ratio between the cross-sectional area of the test cell to the area of the vent line.

For the current test cell design, a vent line diameter of ~2.5 mm yields superficial velocities for most systems (30–60 cm/s); thus, 40 to 60% of the liquid will be left behind following a blowdown transient if nonfoamy behavior prevails (4). On the other hand, if a foam-like regime prevails, essentially no liquid is left behind in the test cell. The superficial velocity is independent of the pressure level. The liquid fraction left behind is insensitive to the discharge flow rate whether it follows nonequilibrium or equilibrium flashing flow behavior. This means a short, 2.5 mm diameter, vent line is adequate over a wide range of conditions.

The test procedure is also straightforward, Figure 5:

- Following onset of tempering, the containment pressure is quickly decreased to ambient condition by opening the exhaust valve, thereby initiating the blowdown process.

- Upon completion of the transient, i.e., when the test cell pressure also reaches ambient condition, the containment exhaust line is closed. Then the containment vessel (and hence the test cell) is immediately repressurized to a level well above the initial set pressure. Any further mass loss from the test cell, due to evaporation, is completely suppressed.

- Following cooldown of the test sample, the mass left in the test cell is obtained by weighing the system.

Using the procedure, the styrene example is clearly shown to be foamy in nature during runaway conditions, Table 1, which is consistent with the large-scale runaway experiments.

Viscosity

Discrimination between turbulent and laminar flashing flow condition is necessary to assess the volumetric vent line flow. If the occurrence of laminar flow is considered a possibility, the bench-scale equipment using a bottom vented test cell and again using the blowdown technique can be used to simulate a runaway reaction in a large process vessel. A vent line with a length-to-diameter (L/D) ratio of ~30 and $L \sim 100$ mm is usually employed to assure equilibrium flashing flow condition (5,6).

The test procedure (5) is straightforward, Figure 6:

- Following onset of tempering, the external bypass valve is closed. (In the open position, pressure equalization between the test cell and the containment vessel is assured.) The containment vessel exhaust valve is then opened, thereby initiating the blowdown process.

- The flow rate is obtained by simply measuring the emptying time (Δt_E), Figure 6. The sharp knee in the test cell pressure-time curve essentially indicates that the vessel is empty of liquid content.

This measured flow rate can be compared to the turbulent two-phase flashing critical flow rate, G , given by (6):

$$G = \frac{dP}{dT} (T/C_p)^{1/2} \quad (1)$$

where

P = vapor pressure
 T = corresponding temperature
 C_p = liquid specific heat

These properties are readily determined from thermal data obtained with a closed system test.

Using the 80% styrene runaway data at the following relief conditions:

$$\begin{aligned} P &= 5.15 \times 10^5 \text{ Pa} \\ T &= 491 \text{ K} \\ C_p &= 2,520 \text{ J/kg}\cdot\text{K} \\ dP/dT^* &= 8,246 \text{ Pa/K} \end{aligned}$$

[* From Figure 7, the P - T relationship for 80% styrene is given by $\ln P(\text{Pa}) = 21.03 - 3,870/T(\text{K})$ and the derivative is given by $(dP/dT) = (3,870)(P)/T^2$.]

the turbulent flow rate becomes

$$G = \frac{dP}{dT} \left(\frac{T}{C_p} \right)^{1/2} = 8,246 \left(\frac{491}{2,520} \right)^{1/2} = 3,640 \text{ kg/m}^2 \cdot \text{s} \quad (2)$$

Since the measured flow rate for the styrene-ethylbenzene system is found to be approximately the same (within 10%), the simple turbulent flow expression, Eq. 1, can be safely used to determine the vent size for the styrene system.

Vent sizing

For pure vapor systems, the above tests provide enough information to allow vent sizing without requiring detailed kinetics and physical property data. This can be accomplished by either using the generalized vent sizing nomogram (based upon 20% overpressure) (7) or a more detailed analytical method to allow for a wider variation in overpres-

Figure 6. Typical depressurization characteristics of tempered systems using bottom venting.

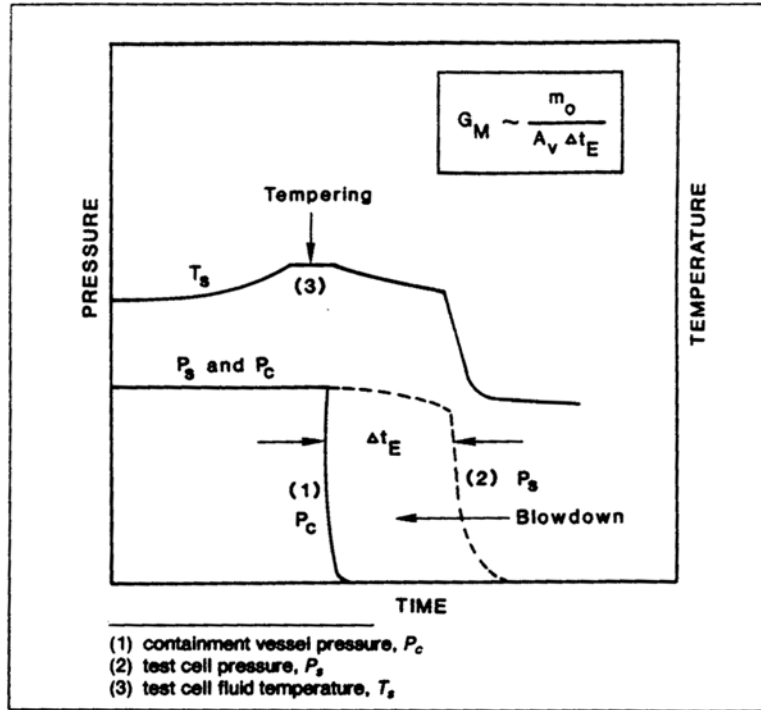


Figure 7. Vapor pressure vs. temperature.

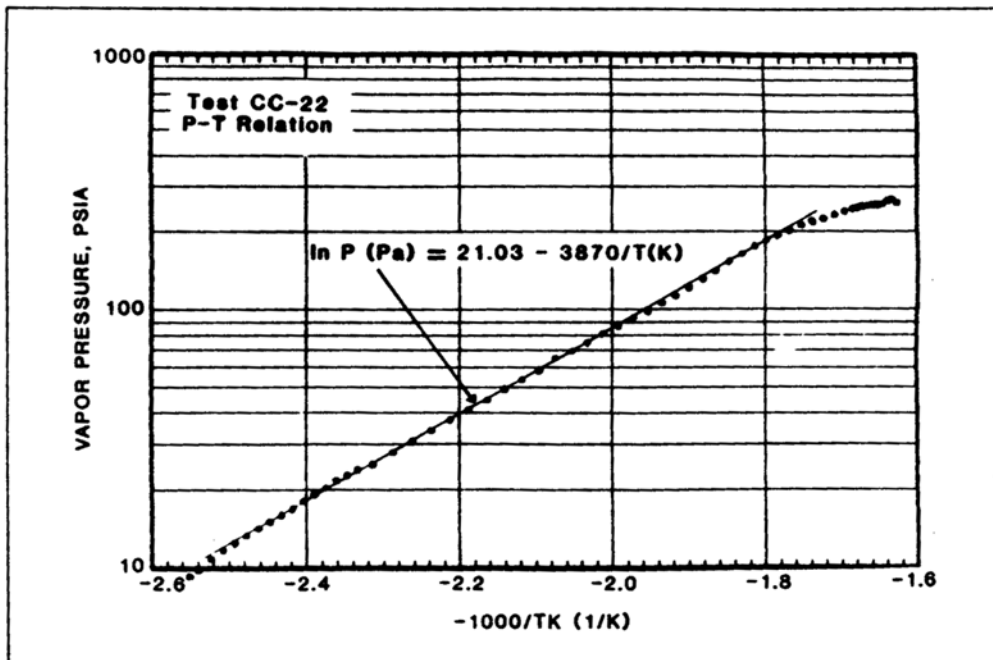


Figure 8. Vent area vs. overpressure (based on gage pressure) for a frictionless vent line: comparison between the analytical model (Eq. 3) and the detailed computer calculations.

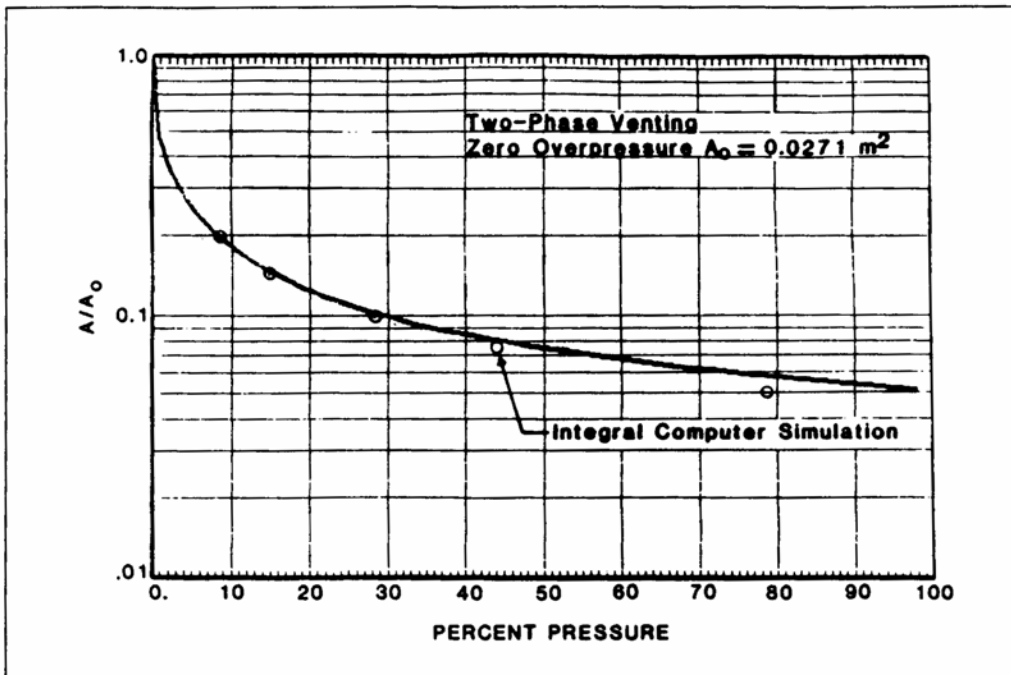
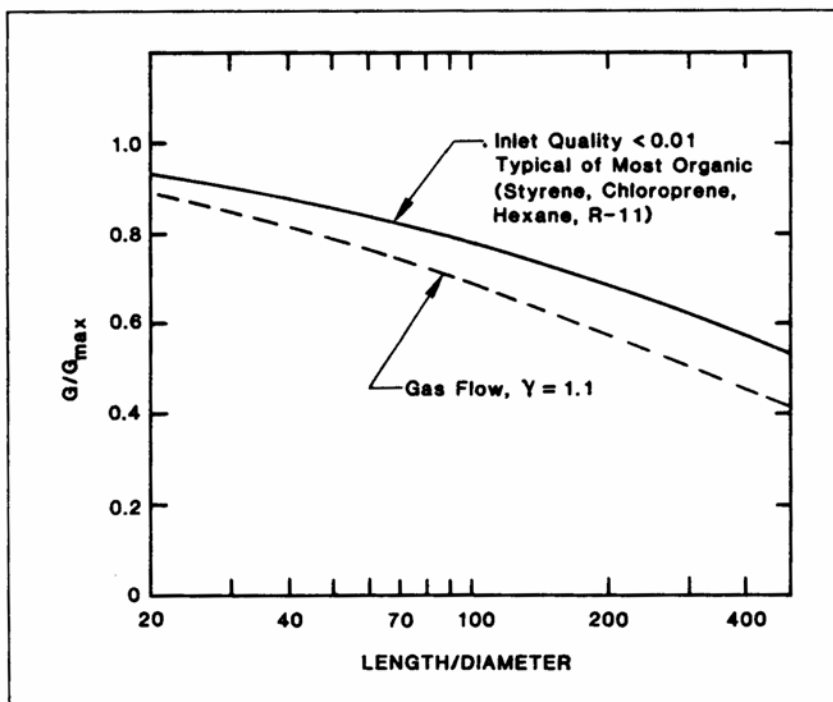


Figure 9. Flow reduction factor vs. length-to-diameter ratio of vent line.



sure, including the zero overpressure case, using the following equation (8):

$$A = \frac{m_o \cdot \bar{q}}{G \left[\left(\frac{V}{m_o} T_s \frac{dP}{dT} \right)^{1/2} + (C_p \Delta T)^{1/2} \right]^2} \quad (3)$$

where

A = vent area (m^2)
 m_o = total charge in the large scale vessel (kg)
 V = vessel volume (m^3)
 T_s = temperature at which the vent opens (K)
 C_p = liquid specific heat (J/kg·K)
 T_m = temperature at pressure turnaround (K)
 dP/dT = temperature derivative of the system vapor pressure evaluated at the set pressure (Pa/K)
 ΔT = temperature equivalent of the overpressure and is given by ($T_m - T_s$) (K)

and the average heat generation rate \bar{q} is evaluated from the relationship:

$$\bar{q} = \frac{1}{2} C_p \left[\left(\frac{dT}{dt} \right)_s + \left(\frac{dT}{dt} \right)_m \right] \quad (4)$$

where $(dT/dt)_s$ and $(dT/dt)_m$ are the self-heat rates ($^{\circ}\text{C/s}$) at the set temperature and turnaround temperature, respectively.

The thermal data obtained for the 80% styrene/20% ethylbenzene system will be used to illustrate the calculational procedures. Since this is a pure vapor system (no noncondensables) and exhibits nonviscous behavior as illustrated above, the vent sizing can be determined using the thermal data alone.

The following reactor parameters corresponding to relief set pressure conditions are used:

$m_o = 5,000$ kg (80% styrene/20% ethylbenzene)
 $V = 7.78$ m^3
 $P_s = 5.15 \times 10^5$ Pa
 $T_s = 491$ K
 $C_p = 2,520$ J/kg·K
 $dP/dT = 8,246$ Pa/K
 $dT/dt = 0.25^{\circ}\text{C/s}$ (15°C/min at 491 K)
 $G = 3,640$ kg/ m^2s

Considering the turnaround point (P_m, T_m) to correspond to 20% overpressure based on absolute pressure, we obtain:

$$\Delta P = 103,000 \text{ Pa}$$

$$\Delta T = 11.6^{\circ}\text{C}$$

and the average energy release rate is given by (values of dT/dt obtained from Figure 4)

$$\begin{aligned} \bar{q} &= \frac{1}{2} C_p \left[\left(\frac{dT}{dt} \right)_s + \left(\frac{dT}{dt} \right)_m \right] \\ &= \frac{1}{2} (2,520) [0.25 + 0.33] \\ &= 735 \text{ W/kg} \end{aligned}$$

The vent area for a frictionless vent line is then given by:

$$\begin{aligned} A &= \frac{m_o \bar{q}}{G \left[\left(\frac{V}{m_o} T_s \frac{dP}{dT} \right)^{1/2} + (C_p \Delta T)^{1/2} \right]^2} \\ &= \frac{5,000 \cdot 735}{3,640 \left[\left(\frac{7.78}{5,000} (491)(8,246) \right)^{1/2} + ((2,520)(11.6))^{1/2} \right]^2} \\ &= 0.016 \text{ m}^2* \end{aligned}$$

(* An identical result is obtained by using the SAFIRE computer code (8) based on measured energy release rates and using physical properties corresponding to the 80% styrene/20% ethylbenzene mixture.)

Figure 8 shows the reduction in vent size from the zero overpressure case as a function of overpressure based on the above calculational procedure. Also shown is a comparison with the detailed SAFIRE computer code.

For cases where a vent line of significant L/D is involved, the actual vent area has to be increased to accommodate the reduction in flow. The flow reduction factor G/G_{max} can be obtained from Figure 9, where G_{max} is the flow corresponding to a frictionless nozzle ($L/D \rightarrow 0$). The reduction factor is shown for two cases including low quality inlet (homogeneous equilibrium model including frictional losses) (6) and all vapor inlet flow conditions. Since the all-vapor case represents the lowest possible flow reduction, its use is recommended to assure a conservative estimate. For the 20% overpressure case and using a vent line of $L/D \sim 100$, the actual vent area (A_a) is indicated as:

$$\begin{aligned} A_a &= \frac{A}{G/G_{\text{max}}} \\ &= \frac{0.016}{0.69} \sim 0.023 \text{ m}^2 \end{aligned} \quad (5)$$

which corresponds to a vent diameter of ~ 17 cm.

The use of the simple nomograph method for the above case (20% overpressure and $L/D \sim 100$) results in a recommended vent diameter of ~ 18.2 cm. Generally, a good first estimate of the vent size can always be obtained by using the nomograph. The analytical procedure of this article is recommended, however, if larger variations in overpressure as well as more detailed consideration of frictional losses for a given vent line are desirable. It is most significant that these predictions were validated by well-instrumented large-scale (2,000 L) runaway reaction and venting tests with the styrene-ethylbenzene system.

In conclusion

The new bench-scale apparatus for characterizing runaway chemical reactions can handle largely unknown systems with a small test cell (~ 100 mL). This allows direct and safe extrapolation to large scale at relatively low cost. In terms of vent sizing, nothing needs to be known about the system to be tested—not even the identities of the chemicals involved. Given the upset condition, the new method allows for the first time safe extrapolation to full-size process vessels.

The unique test cell design with an adiabaticity factor approaching 1 also provides reliable thermal data including determination of the onset of thermal instability, temperature of no return, and time to maximum rate.

Other unique features include flow regime characterization to distinguish between foaming and nonfoaming vessel behavior and viscosity characterization to distinguish between laminar and turbulent flashing flow conditions under actual runaway process conditions. #

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