Multi-Phase Flow Considerations in Sizing Emergency Relief Systems for Runaway Chemical Reactions

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ABSTRACT

Based upon available literature data recommendations are made as to the choice of two-phase flow models to assure an adequate emergency relief system (ERS) design. For large process vessels and in the absence of flow regime characterization data under runaway conditions, a safe ERS design requires consideration of homogeneous vessel behavior and vent line flow characteristics based upon homogeneous equilibrium flow. For the majority of cases this approach may in fact represent a best estimate assessment.

1. INTRODUCTION

Emergency relief systems for pressure vessels are being used extensively in the chemical industry to minimize the potential for chemical explosions and extensive spreading of hazardous material. In addition to uncertainties related to chemical kinetics data in general, the possibility of flashing flow occurring in the relief device and its potential effect on the vent size is of particular interest* [1].

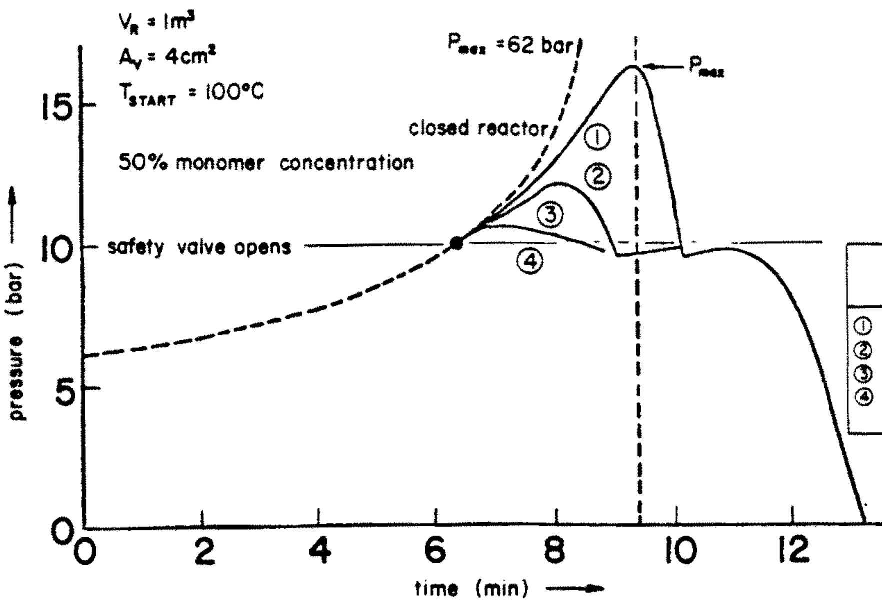
The question of vapor venting versus liquid-vapor venting depends upon the prevailing flow regime, such as bubbly, churn turbulent or droplet flow, which is generally not known during runaway conditions. In addition, the nature of the venting process is likely to be strongly influenced by the general problem of "foaming" which is aggravated by the presence of certain additives or emulsifiers and is known to be highly dependent on the particular system properties and minute quantities of impurities. In view of this highly variable picture, it is not surprising that a number of calculational methods have been published concerning sizing of emergency relief systems for runaway chemical reactions [2]. These methods include all-vapor venting, all-liquid venting [3], vapor-liquid venting with no vapor disengagement, i.e., homogeneous vessel behavior [4, 5, 6] and vapor-liquid venting with vapor disengagement, i.e., churn turbulent vessel behavior [7].

A similar status exists for describing the flow through the relief device [2]. These methods all-vapor flow, all-liquid flow without flashing [3], homogeneous equilibrium flashing flow [1, 4, 5], frozen flow [6], non-equilibrium flashing flow [7], and slip equilibrium flashing flow [4, 6]. It follows that a significant variation in the vent size can be obtained depending upon the choice of modeling the vessel behavior, (i.e., the degree of vapor disengagement) and the vent line flow dynamics, (i.e., the two-phase critical flow). The variation in overpressure for a given vent size as a function of flow model assumed is illustrated in Fig. 1. Particularly noteworthy is the sizable reduction in overpressure resulting from assuming either all vapor venting or non-equilibrium flow (frozen quality) relative to assuming equilibrium flashing flow. These aspects are discussed further below with the objective of providing definitive recommendations as to the choice of models to assure a safe but not overly conservative emergency relief design.

2. VAPOR DISENGAGEMENT

The liquid and vapor motion inside a reaction vessel during pressure relief is a complex hydrodynamic problem. Fauske, Grolmes and Henry [7] have recently presented a first order method to predict liquid swell and partial disengagement which has been verified for one-component, non-reacting systems such as water, (i.e., non-viscous and non-foaming). Figure 2 illustrates typical capability of integral analysis [8] incorporating vapor disengagement based upon churn behavior [7] and non-equilibrium flashing critical flow [9] to predict Freon-12 depressurization experiments reported in Ref. [10]. Significant deviations from both homogeneous vessel behavior

* Generally speaking, a smaller vent is needed to handle all-vapor flow than a two-phase mixture.



	liquid entrainment in the reactor	flow in the ventline	
		phase slip	thermodynamic state
1	yes, foaming	no	equilibrium
2	yes, foaming	$\frac{u''}{u'} = \left(\frac{\rho'}{\rho''}\right)^{1/3}$	equilibrium
3	yes, foaming	no	frozen quality
4	no, relief of vapor	no	equilibrium

Fig. 1 Typical pressure-time curves calculated for a runaway polymerization reaction, including all-vapor and homogeneous (foaming) venting assumption. Vent flow model assumptions include homogeneous equilibrium, slip equilibrium and non-equilibrium (frozen quality) conditions. (Taken from Ref. [6].)

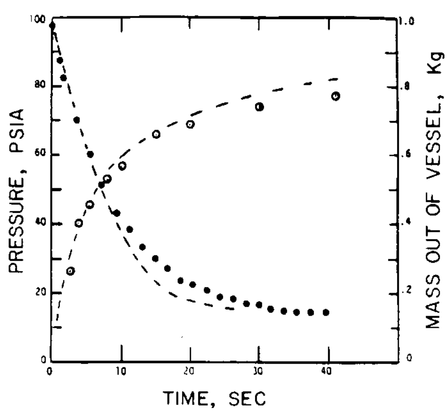


Fig. 2 Comparison between integral analysis and depressurization data with Freon-12 using top venting (nozzle size 4.6 mm).

as well as equilibrium flashing vent flow* are required in order to predict such data.

However, significant vapor disengagement would appear to be absent with many chemical systems because of the inherent "bubbly" and/or "foaminess" as well as high viscosity, giving rise to homogeneous two-phase flow like behavior throughout most of the venting sequence. For example, Howard has stated (see Ref. [4]) that an industrial vessel containing a 10 cp monomer discharges once or twice a year through an adequately designed relief system and only 25-30% of the liquid mass remains in the vessel at the end of blowdown. Reference [3] also reports actual case histories of polymerization kettles containing up to 4,000 gal. of reacting monomers and water which were relieved of their contents (completely emptied) through the emergency relief line. Finally, incidents reported by Burchett [11] involving runaway reactions of chloroprene in large process vessels which are interpreted in the concluding portion of this paper suggest a similar behavior, i.e., a nearly homogeneous-like venting behavior. Even small test vessels in some instances indicate little or no vapor disengagement. Harmon and Martin [12] experimented with various polymerization reactions at high monomer concentrations in a 5-gal. vessel. For those runs with an adequate relief system they reported only 0-20% liquid retention at the end of blowdown. Boyle's experience working with a polystyrene solution in ethylbenzene (1-quart volume) lead him to suggest the all-liquid venting model [3]. Huff [13] examined visually the liquid-vapor interactions in gallon-size polystyrene/ethylbenzene solutions and concluded that a zero vapor disengagement assumption "is quite realistic over much of the course of the discharge from polymerization reactors." It follows that a safe emergency relief design approach must consider a homogeneous liquid-vapor mixture entering the vent line, unless flow regime characterization data are available for a given system under

* Significant deviation from equilibrium flashing flow in this case is closely related to the aperture geometry in question, (i.e., short nozzle and is discussed in further detail in Section 3 of this paper.

prototypic runaway relief conditions which demonstrate significant vapor disengagement*.

3. TWO-PHASE CRITICAL FLOW

Model selection for predicting critical flow of flashing two-phase mixtures requires consideration of non-equilibrium effects [9]. Required relaxation lengths to approach equilibrium flow conditions have been demonstrated in a number of experiments reported in the open literature. In 1964 Fauske [14] illustrated the effect of geometry upon the critical flow rate for saturated water and a very wide range in the stagnation pressure, (see Fig. 3). The rapid decay in flows prior to reaching the asymptotic values [length-to-diameter (L/D) radio of approximately 16] were attributed to increasing fluid residence times. For an L/D = 0 (sharp edged orifice), the residence time is zero resulting in no flashing and the flow rate can be predicted by the standard incompressible single-phase flow equation [14]. On the other hand, at L/D approximately 16 sufficient time is available to allow the flashing process to approach equilibrium. The relatively small decreases in the flow rates noted for larger L/D's were attributed mostly to frictional effects. For the given tube diameter (D = 6.35 mm, these experiments suggest an essentially constant relaxation length of the order of 100 mm over a wide range in the stagnation pressure.

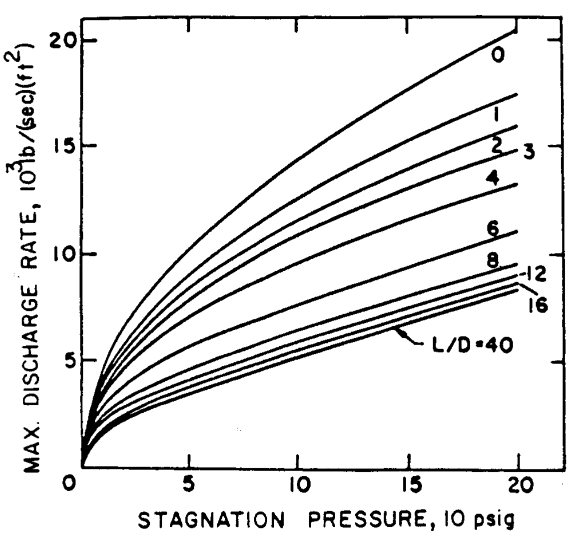


Fig. 3 Maximum discharge rates of saturated water for 0.25-in. I.D. tube [14].

A similar trend in the critical flow behavior starting from saturated or inlet quality conditions in terms of flow geometry dependency have been noted by Sozzi and Sutherland [15], Flinta [16], Uchida and Nariai [17] and Fletcher [18]. These experiments are summarized in Table 1 in terms of LD ratios and relaxation lengths corresponding to a change to equilibrium critical flow behavior. Table 1 clearly shows that the L/D ratio does not correlate the relaxation process, while a simple length criterion of the order of 100 mm appears to characterize the residence time requirement for both tubes and nozzles covering wide variations in diameter and stagnation pressure including different fluid properties such as water and Freon-11.

Table 1

ILLUSTRATION OF RELAXATION LENGTH, L OBSERVED IN DIFFERENT CRITICAL FLOW EXPERIMENTS

Source	D, mm	L/D	L, mm
Fauske (water)	6.35	~ 16	~ 100
Sozzi and Sutherland (water)	12.7	~ 10	~ 127
Flinta (water)	35	~ 3	~ 100
Uchida and Nariai (water)	4	~ 25	~ 100
Fletcher (Freon-11)	3.2	~ 33	~ 105
Marviken Data (water)	500	< 0.33	< 166

Further support for the simple criterion is provided by the recent large scale Marviken data with inlet quality conditions [19]. For a nozzle diameter of 500 mm, relatively little change is observed in the critical flowrate when the L/D ratio is varied from 0.33 to 3.2 (see Table 2). It is particularly noteworthy that the predicted homogeneous equilibrium model (HEM) critical flow rate* is only about 10% lower than the observed flow rate at L/D = 0.33, suggesting that the relaxation length for the 500 mm nozzle also is of the order of 100 mm.

Table 2

MARVIKEN DATA - SATURATED FLOW
D = 500 mm, P_o ~ MPa

Critical Flow Rate kg/m^2 x 10^{-3}	L/D
~ 24.5	~ 0.3
~ 23.3	~ 1.5
~ 22.0	~ 3
HEM → 21.7	-

* Significant vapor disengagement implies that a sizable fraction of the contents in a large process vessel would remain in the vessel following blowdown. It is noted that top venting in a small test vessel can be quite misleading in this regard, since the entrainment velocity is directly proportional to vessel height [7].

* This model can be described by the same equations as an equivalent single-phase flow. The two phases are everywhere in equilibrium with equal velocities and temperatures. At low qualities the HEM critical flow rate can be estimated within 10 to 15% from $[h_{fg}\ \rho_g\ (cT)^{-1/2}]$ where h_{fg} is the latent heat of vaporization, ρ_g is the vapor density, c is the specific heat and T is the temperature, all properties evaluated at the stagnation condition. For further details see Ref. [20].

In fact, excellent agreement between the HEM predictions based upon stagnation properties and the experimental data is noted for reduced critical pressure (P/Pc where Pc is the thermodynamic critical pressure) of the order of 0.1 and above which is the range of interest for most chemical systems (see Figs. 4 and 5).

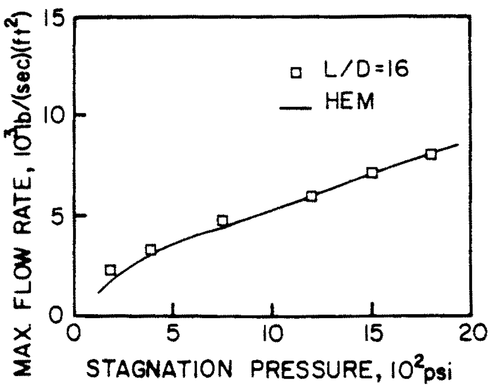


Fig. 4 Comparison between measured [14] critical flow rates (L ~ 100 mm) and the homogeneous equilibrium model (HEM) elevated for stagnation conditions.

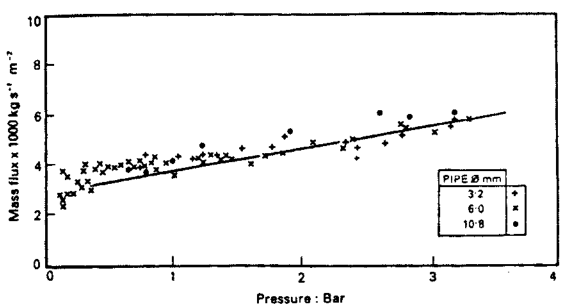


Fig. 5 Effect of pipe diameter on mass flux through a pipe of length 120 mm [18] and comparison with the HEM predictions (solid line).

Since sizing of emergency relief systems for runaway chemical reactions generally involve inlet quality conditions and relatively large flow devices, the above criterion suggests that a safe as well as a best estimate prediction of the critical flow rate should be based on the HEM.

4. CONCLUDING REMARKS

For large process vessels and in the absence of flow regime characterization data under runaway conditions, a safe emergency relief system design requires consideration of homogeneous vessel behavior and vent line flow characteristics based upon homogeneous equilibrium flow. For the majority of cases this approach may in fact reflect a best estimate assessment.

An example at hand is the two incidents of runaway reaction of chloroprene in large scale vessels reported by Burchett [11]. The first incident involved a 3000-gallon reaction vessel with a 30 psig, 4 in. diameter safety disc and an equivalent sized tailpipe. The vessel vented safely, and following the incident the vessel was found to be essentially empty. The second incident involved a 2000-gallon vessel again with a 4-in. diameter safety disc (and an equivalent sized tailpipe) but set at 75 psig. In this case the runaway reaction resulted in vessel rupture. Using Burchett's measured energy release rates for the cholorprene system [11], the predicted pressure behavior for the two vessels is illustrated in Fig. 6. Assuming the 4-in. relief device is fully available for venting, (i.e., ruling out any polymer deposits on the disc and/or partial plugging of the relief line), homogeneous venting (homogeneous vessel behavior and homogeneous equilibrium vent flow) is clearly suggested by the observed behavior. The 3000-gallon reaction vessel is predicted to vent safely while an explosive pressure runaway condition cannot be ruled out for the 2000-gallon reaction vessel. On the other hand, assuming churn turbulent vessel behavior [7], (i.e., significant vapor disengagement) clearly suggests that the 2000-gallon vessel also should have vented safely.

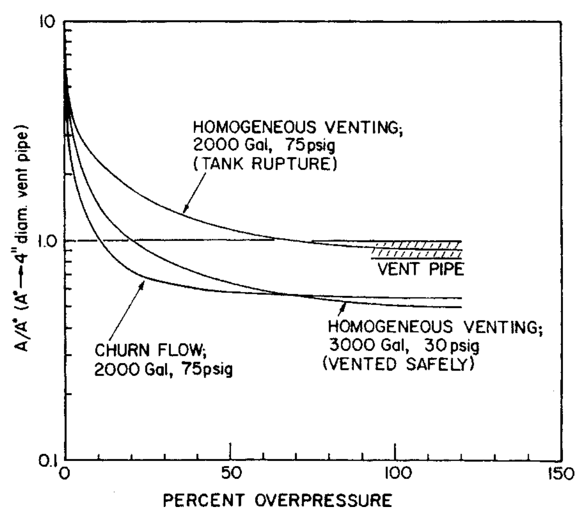


Fig. 6 Predicted pressure behavior of two reported incidents involving runaway reaction of chloroprene in large scale vessels. Shaded band represents the estimated uncertainty in the actual discharge coefficient for the incident vent line. Calculations performed with a discharge coefficient equal to 1.0.

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