Runaway reaction
Validating a less overestimating vent sizing method

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Abstract

Simplifying assumptions used in DIERS classical vent sizing methods for gassy systems (mainly conservation of the initial reactive mass and homogeneous vessel venting) can lead to unrealistically large vent areas. H. Fauske (2000) proposed to use the same vent area as for pure gas flow venting. It thus leads to a much smaller vent area. This paper deals about our understanding of Fauske's method bases by introducing the "balance idea": when changing from one phase to two-phase venting, decrease of mass inventory in the reactor could balance venting velocity decrease. Theoretical testing of this idea allowed us to identify types of systems for which this approach could potentially be not conservative. One is when the reaction kinetics are already rapid at vent opening and there is therefore not much time for mass to vent before turn-around. Another is when high quality vent flow occurs (gas with small fraction of liquid) so that vented mass is relatively small, vent flow velocity at vent being however severely decreased compared to pure gas velocity.

Keywords : vent sizing method ; gassy reaction ; runaway reaction ; gas venting flow

I. Introduction

Vent sizing methods were based for a long time on the assumption of one-phase venting (vapor/gas). Thanks to the DIERS (Design Institute for Emergency System Relief), these methods evolved to the use of simple analytical models (and complex computer codes) which take the occurrence of two-phase flow into account (Leung, Fauske 1987). These methods use data obtained from adiabatic calorimetry.

Nevertheless, because of simplifying assumptions (mainly conservation of the initial reactive mass and homogeneous vessel venting), DIERS methods can lead to unrealistically large vent areas. This is especially the case for untempered systems (gas-generating and hybrid systems, peroxide decomposition for example).

From large scale experiments, Fauske (2000) proposed to use the same vent area as for pure gas flow venting. It thus leads to a much smaller vent area.

The objective of this paper is twofold. The first is to propose our understanding of Fauske's method bases : when changing from one-phase to two-phase venting, decrease of mass inventory in the reactor could balance the venting velocity decrease.

The second objective is to verify whether this balance phenomenon can always apply or not. We tested this approach with a gassy system example by a computer simulation, which takes both the vented mass loss and the venting volume flow rate decrease into account. The calculation allowed us to identify types of systems for which this approach could potentially be non conservative.

II. Basis of vent sizing for gassy systems; origin of oversizing

The vent sizing method for gassy systems is based on two balances: total mass balance and gas mass balance (Leung 1995).

$$\frac{dm}{dt} = -W = -GA \qquad \textbf{Equation 1}$$

$$\frac{dm_g}{dt} = m\dot{m}_g - Wx_i \qquad \textbf{Equation 2}$$

Safe vent size is obtained if the pressure rise can be stopped when the gas generation rate is maximum. This leads to consider a pressure rise rate equal to zero. This condition is often called the turn-around :

$$\frac{dP}{dt} = 0 \qquad \textbf{Equation 3}$$

By assuming ideal gas and constant liquid specific volume, recombining equations 1 to 3 leads to the following expression for the vent area $A_{2\varphi}$:

$$W_{2\varphi} v_{i2\varphi} = A_{2\varphi} \left(G_c \; v_i\right)_{2\varphi} = v_g m \dot{m}_g + \frac{v_g m_g}{T}\left(\frac{dT}{dt}\right)$$

Equation 4

Where $v_i = x_i v_g + (1 - x_i) v_l$

x_i : vent flow quality (gas mass fraction) at inlet condition

v_g : gas specific volume in the reactor.

All terms in equation 4 have to be evaluated at turn-around. So this equation means that at turn-around the volumetric discharge rate is equal to the sum of:

- volumetric gas generation rate
- volumetric expansion rate due to thermal dilatation. We will subsequently neglect this term as is generally done.

Equation 4 contains three factors which are not known. G_c, v_i and m at turn-around. In order to allow for vent sizing even when these important data are lacking, DIERS methods make the following safe assumptions:

- All the initial mass is still present in the vessel at turn-around (Leung, Fauske, 1987)
- Homogeneous two-phase flow with homogeneous vessel contents occurs at turn-around (Leung, 1995) or even Bernoulli flow occurs when void fraction is low (Leung, Fauske, 1987).

The DIERS vent sizing formula resulting from the above assumptions is given by:

$$A_{DIERS} = \frac{1}{\left(G_c v_i\right)_{HEM\,\mathrm{hom}}} v_g m_0 \dot{m}_g$$

Equation 5

Unfortunately this equation can lead to vent oversizing. For example, in the case of peroxide decomposition runaway reaction, vent area obtained from this vent sizing method can be overestimated by one order of magnitude (Fauske 2000). Moreover, experience showed that smaller vent size can provide good protection against runaway reaction.

$$\frac{A_{DIERS}}{A_{2\varphi}} = \left(\frac{\left(G_c v_i\right)_{2\varphi}}{\left(G_c v_i\right)_{HEM\,\mathrm{hom}}}\right)\left(\frac{m_0}{m}\right)$$

Equation 6

Equation 6 shows that the possible ways for solving this problem are: a better assessment of $\left(G_c v_i\right)_{2\varphi}$ and the remaining mass at turn-around m. In fact, these data are not experimentally available. Fauske (2000) proposed an interesting way to solve this oversizing problem.

III. Fauske's method and balance idea

For gassy systems, Fauske (2000) simply proposed to install the same vent area as for pure gas flow (A_{gas}). Equation 4 neglecting vented gas mass then becomes:

$$A_{\mathrm{gas}} = \left(\frac{1}{G_{c\,gas}}\right)\left(m_0 \dot{m}_g\right) \qquad \textbf{Equation 7}$$

He verified from large scale data (33 to 2000 liters) about peroxide systems (3,5,5-Trimethyl Hexanoyl Peroxide, Neat Dicumyl peroxide and t-Butyl Peroxy Benzoate) that this area is safe (Figure 1).

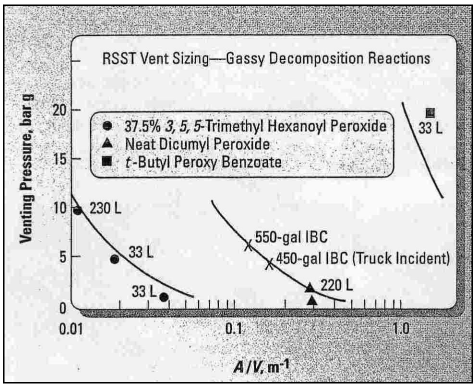

Figure 1 : Large scale runaway peroxide decomposition data ; comparison with gas vent area after Fauske (2000)

Fauske also pointed out (as indicated by calorimetric test) that significant material losses occurred before reaching turn-around.

So the large scale experiments show that even if two-phase flow obviously occurs, vent design for gas only flow is safe. This method can seem at a first sight non conservative compared to the classical DIERS method (Equation 5). But experiments show its efficiency. We tried to give a theoretical explanation to this idea.

If one phase flow actually occurs this method is right. Two phenomena occur concurrently when changing from one-phase flow to two-phase flow:

- vent flow velocity decreases, which tends to ask for a vent area increase.
- mass vented at turn-around increases, which tends to ask for a vent area decrease.

Validity of Fauske's proposal (use gas area even when two-phase flow occurs) could result from a balance between these two phenomena. That's what we called the "balance idea". This idea is mathematically expressed by the vent area needed when two-phase flow occurs being less or equal to the vent necessary when one phase flow occurs:

$$A_{2\varphi} \leq A_{\mathrm{gas}} \qquad \textbf{Equation 8}$$

Combining equation 4, 8 and 9 the condition for balance idea to be correct is the following:

$$\left(\frac{m}{m_0}\right) \leq \left(\frac{(G_c v_i)_{2\varphi}}{(G_c v_i)_{gas}}\right) \qquad \textbf{Equation 9}$$

This condition means that the vent area decrease effect due to mass loss has to be more or equal to the vent area increase effect due to the decrease of the flow velocity when changing from gas to two-phase flow.

IV. Test of balance idea

Our aim is now to verify if equation 9 is always valid. Unfortunately not enough large scale data are available in order to demonstrate it. This lead us to use simple models in order to identify cases where balance idea could potentially not apply. This approach thus allow for *qualitative only* study.
We took gassy reaction data from Etchells *et al.* (1998). They are described in Table 1.

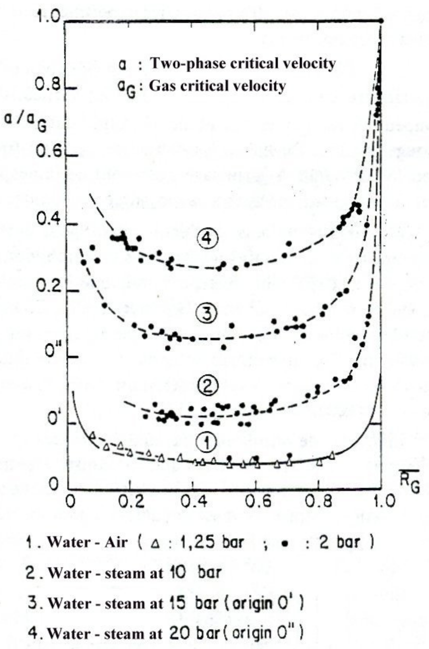

Figure 2 : Two-phase to gas critical velocity ratio vs void fraction (Semenov and Kosterin, 1964)

IV.1 Two-phase flow model

We are looking at the $(G_c v_i)_{2\varphi} / (G_c v_i)_{gas}$ ratio. We show in appendix that this ratio can be approximated by the two-phase to gas critical velocity ratio : $u_{c2\varphi} / u_{cgas}$.
Figure 2 shows experimental data for this latter ratio. We also assessed the $(G_c v_i)_{2\varphi} / (G_c v_i)_{gas}$ ratio versus α_i , using both Leung's ω-method (1990) and Tangren *et al.* method (1949).
The shape of the curve in Figure 3 is in accordance with the experimental data (Figure 2). This justifies the subsequent use of these models.

IV.2 Graphical representation of balance idea

Conditions of validity

As explained in III. , validity of balance idea needs equation 9 to be verified for a vessel equipped with a vent sized for gas flow. Figure 3 can be read as the graphical representation of this condition.
For a given two-phase flow void fraction at turn-around α_i , m/m_0 ratio has to lie below the $(G_c v_i)_{2\varphi} / (G_c v_i)_{gas}$ curve. On the contrary, if m/m_0 ratio lies above the curve, the vented mass is not sufficient to balance the vent flow velocity decrease. So vent area assessed by one phase flow calculation would be undersized.

Effect of mass loss on the balance

Figure 3 also represents two extreme cases: 20% and 80% of remaining mass in the large scale vessel at turn-around.
For the unfavourable value of 80%, the curves show that even a little volume fraction of liquid in the evacuated flow at turn-around (3% for example) would lead to balance idea being not verified. Balance would only occur if void fraction is more than 98%. So sizing the vent by assuming one phase flow could be unsafe.

Vessel	Vessel volume	3.5 m^3	Vent opening pressure	14 bars
	Initial mass inventory	2500 kg	Maximum allowable pressure	16 bars
Calorimeter	Gas phase volume	3.8 l	Maximum pressure rise rate	2263 N/m².s
	Sample mass	44.8 g	Maximum temperature rise rate	6.95 K/s
	Maximum reactant contents temperature in the test cell	519 K		

Table 1 : Gassy reaction data ; example from Etchells *et al.* (1998)

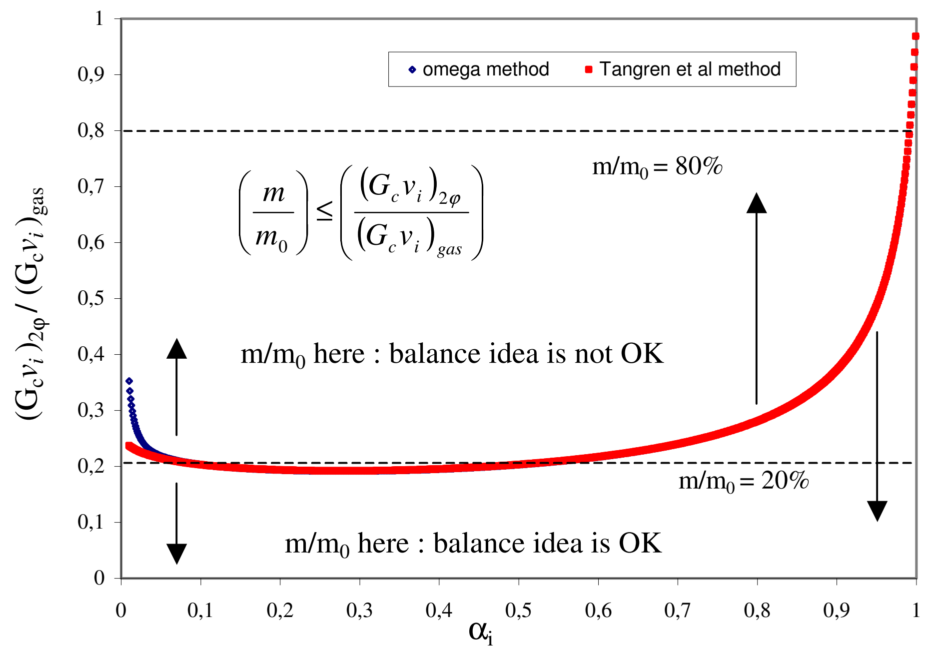

Figure 3 : Ratio $(Gv_i)_{2\varphi}/(Gv_i)_{gas}$ as a function of inlet void fraction by ω-method and Tangren *et al* method ; Conditions of validity of the balance idea

On the opposite the 20% remaining mass case (considered as the favourable case) would balance the fluid velocity decrease whatever the inlet void fraction at turn-around. So sizing the vent as for one phase flow would be a safe method.
This simply means that the value of the ratio of mass remaining at turn-around to initial mass is of primary importance for the balance idea to be verified or not.
Another way for illustrating this fact is to plot the calculated vent area needed when two-phase flow occurs by means of equations 4, 5 and 7.

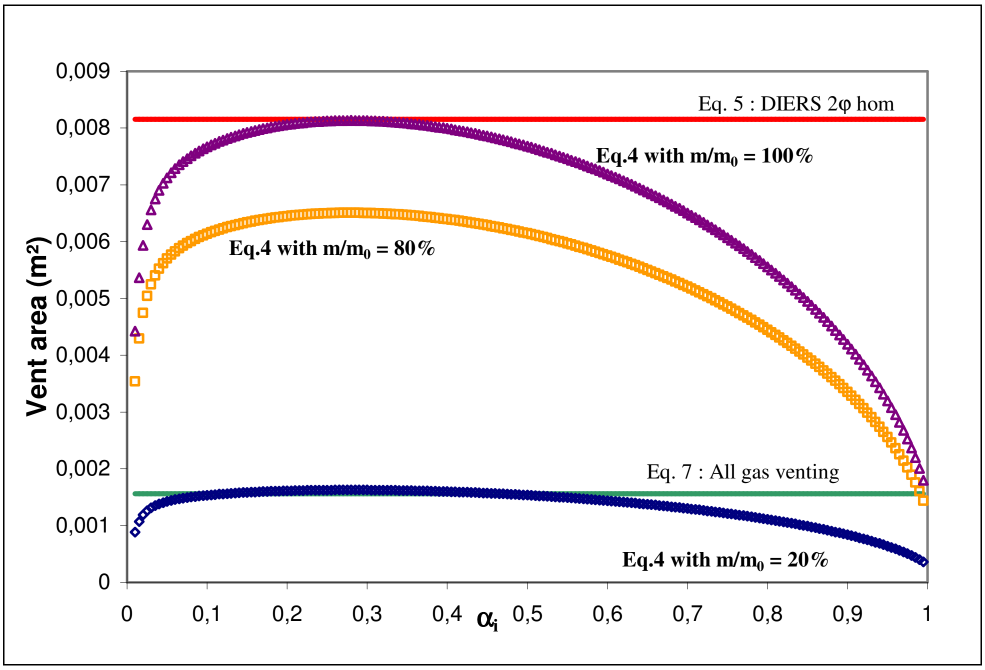

Figure 4 : Vent area as a function of the void fraction for a remaining reactant mass of 20, 80 and 100%

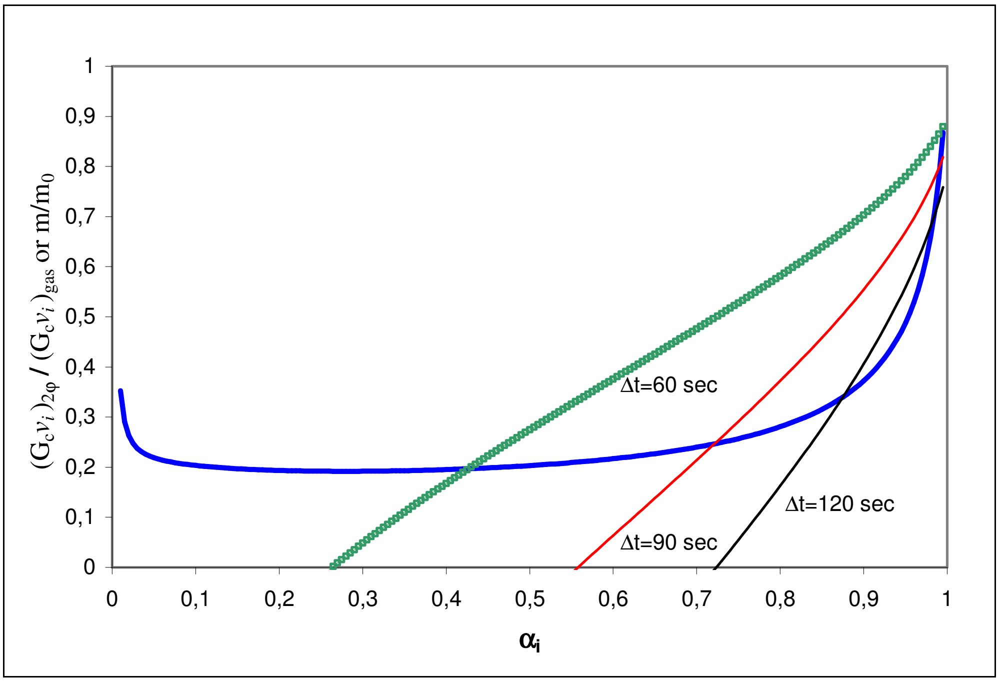

Figure 5 : Conditions of validity of the balance idea when the remaining mass is calculated

We consider here the value of the remaining mass as a parameter. $(G_c v_i)_{2\varphi}$ is calculated versus inlet void fraction by Leung's ω-method (1990). Figure 4 shows the influence of the void fraction on the vent area for remaining reactant masses of 20%, 80% and 100%.

For the 20 % remaining mass case, we can point that :

- balance idea is valid: gas vent size seems to be a safe one.
- DIERS classical vent sizing method (equation 5) is overly conservative.

For the 80% and 100% remaining mass cases, we can observe that :

- balance idea is not valid: gas vent size seems to be unsafe.
- use of DIERS classical vent sizing calculation would have been a safer choice.

IV.3 Link between m and α_i.

Up to now, we supposed that vent void fraction and mass loss at turn-around are independent parameters. It is not completely true: the higher the inlet mean void fraction, the less the mass loss. This link can only be calculated if more assumptions are made.

Vented mass model

We will now assume that:

- G_c is constant during relief (calculated by HEM method at vent opening conditions).
- α_i is constant (no change in the vent flow gas volume fraction) during relief.

Let's express the remaining mass in a vessel equipped with a vent sized for gas flow (A_{gas}):

$$m = m_0 - G_c A_{gas} \Delta t \qquad \textbf{Equation 10}$$

where Δt is the delay between vent opening and turn-around.

Results

Figure 5 presents again the $(G_c v_i)_{2\varphi} / (G_c v_i)_{gas}$ ratio calculated by ω-method versus inlet void fraction. The m/m_0 ratio, calculated thanks to equation 10, is also represented versus inlet void fraction for three values of Δt : 60, 90 and 120 seconds.

We can make the following observations:

- For Δt = 60 seconds, if inlet void fraction in the venting flow is larger than 43%, then mass loss is not sufficient for balance idea to be verified.
- For Δt = 120 seconds, even inlet void fraction as high as 87% will allow balance idea to be verified. But very high inlet void fractions (88%<α_i<98%) could potentially give rise to unsafe conditions.

The kinetics of a gassy reaction are generally supposed to be the same whether the reactor is vented or not. Delay between vent opening and turn-around, Δt is only a function of vent opening pressure.

As a conclusion, it's possible to identify two cases for which the balance idea could potentially not apply:

- When the reaction kinetics are already rapid at vent opening and there is not much time for mass to vent before turn-around.
- When high void fraction vent flow occurs (gas with small fraction of liquid) so that vented mass is relatively small, the vent velocity being however severely decreased.

Discussion about assumptions

Our assumptions (constant G_c and α_i) can be not realistic, even if they are favourable to balance idea because mass loss is probably overestimated compared to what actually happens in the reactor:

- actual pressure will decrease when opening the vent and so that the critical mass flux
- actual void fraction will probably be not constant during Δt. It depends on several factors such as the vent opening pressure, the vent area, etc.

These assumptions however allowed us to qualitatively identify cases for which the balance idea could potentially be unsafe.

V. Conclusion

In this work we exposed our understanding of Fauske's method bases by introducing the "balance idea": when changing from one-phase to two-phase venting, decrease of mass inventory in the reactor could balance the venting velocity decrease.

Testing of this idea using simple models allowed us to identify conditions for which this approach could potentially be not conservative. One is when the reaction kinetics are already rapid at vent opening and there is not much time for mass to vent before turn-around. Another is when high quality vent flow occurs (gas with small fraction of liquid) so that vented mass is relatively small, the venting velocity being however severely decreased.

We still have to verify if balance idea remains safe even under such circumstances. This will be our next experimental investigations.

Nomenclature

A :	Vent area (m²)
G_c :	Critical vent mass flux (kg/m².s)
m :	Remaining mass in the vessel at turn-around (kg)
m_g :	Gas mass (kg)
$\dot{m}_g$:	Specific gas generation rate (kg_{gas}/kg.s)
P :	Pressure in the vessel (Pa)
T :	Temperature in the vessel (K)
u_c :	Critical venting velocity (m/s)
v_c :	Specific volume of the vent flow at critical conditions (m^3/kg)
v_g :	Gas specific volume at vessel conditions (m^3/kg).
v_i :	Specific volume at inlet conditions (m^3/kg)
v_l :	Liquid specific volume (m^3/kg).
W :	Vented mass flow (kg/s)
x_i :	Vent flow gas mass fraction at inlet condition
α_i :	Void fraction at inlet conditions
Δt :	Delay between vent opening and turn-around (s)

Subscripts

c :	Critical conditions
gas :	Gas flow
HEM :	Homogeneous equilibrium model
hom :	Homogeneous vessel contents
0 :	Initial conditions
2φ :	Two-phase flow

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Appendix : $u_{c2\varphi}/u_{cgas}$ as an approximation for $(G_c v_i)_{2\varphi}/(G_c v_i)_{gas}$

From definition of G_c :

$$\frac{(G_c v_i)_{2\varphi}}{(G_c v_i)_{gas}} = \frac{u_{c2\varphi}}{u_{cgas}} \frac{(v_i/v_c)_{2\varphi}}{(v_i/v_c)_{gas}}$$

Except for very low vent quality, we can write:

$$(v_i / v_c)_{2\varphi} \approx \frac{v_{g2\varphi i}}{v_{g2\varphi c}} \approx \frac{(T/P)_{2\varphi_i}}{(T/P)_{2\varphi c}}$$

The inlet critical ratio $\left(\frac{T}{P}\right)_i \Big/ \left(\frac{T}{P}\right)_c$ is not so different, whether the flow is 2φ or gas.

The maximum discrepancy comes from the pressure ratio ($\eta \approx 0.5$ for gas ; $0.5 < \eta < 1$ for 2φ-flow).

$u_{c2\varphi} / u_{cgas}$ can not differ of $(G_c v_i)_{2\varphi} / (G_c v_i)_{gas}$ by more than a factor of two.