The *Batch-size* approach to a safer use of batch and semi-batch reactors

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Small and medium enterprises (SMEs) main feature is to run batch and semi-batch processes, working on job orders. They generally have multipurpose reactors, with an emergency relief system (ERS) already installed. These are normally sized when the reactor is designed, assuming as worst incidental scenario a single phase vapour flow generated by a fire developed outside the apparatus. These assumptions can lead to a big underestimation of the vent area if the actual flow is two-phase and besides generated by a runaway reaction. ERS sizing is particularly hazardous and complex for small mills, as for example fine chemicals and pharmaceutical companies. These factories have usually narrow financial and personal resources, moreover they often use fast processes turnovers. In many cases a complete safety study or the replacement of the ERS is not possible and it can lead to not sustainable costs. The batch-size approach is focused on discontinuous process conditions: aim of this approach is to find the reactor fill level that can lead to a vapour single phase flow whether an incident occurs, this condition is considered safe that the ERS installed on the reactor can protect the plant from explosions.

1. Introduction

Two-phase relief flows can lead to underestimations of the ERS especially for multipurpose reactors. The increase of runaway phenomena in an industrial reactor may cause physical explosions of the reactor (Cardillo, 1998). ERS are traditionally sized when the reactor is designed, assuming as worst incidental scenario a single phase vapour flow generated by a fire developed outside the apparatus. Generally for a vapour process the vent area for a multi phase flow is ten times greater than for a single phase flow. So the assumptions of a singe-phase flow can lead to a big underestimation of the vent area if the actual flow is two-phase and also generated by a runaway reaction. Aim of the batch-size approach is find the reactor fill level that can lead to a vapour single phase flow.

2. Instrumentation

2.1 Adiabatic calorimeter PHI-TEC II

Experimental instruments and mathematical methods for the vent sizing have been studied for more than 30 years by the Design Institute of Emergency Relief Systems (DIERS). As conclusion of these studies, the best instruments to collect proficiency data for vent sizing are adiabatic calorimeters with low thermal inertia, as for example PHI-TEC II (Singh, 1989).

PHI-TEC II oven is made by three different heaters (i.e. top, side and bottom heaters) whose main task is to keep a uniform cell heating (see Figure 1). The sample cell is a

steel can with thin walls (approximately 0,15 mm thick) and a volume of about 110 cm^3. A too large pressure difference between sample and vessel could damage the cell. In order to avoid this, PHI-TEC II is equipped with a pressure compensation system that maintains the differential pressure around unit values. The big can volume leads to remarkable improvements in the reaction conditions: we can load a considerable amount of sample and change the fill level in order to simulate various incidental scenarios.
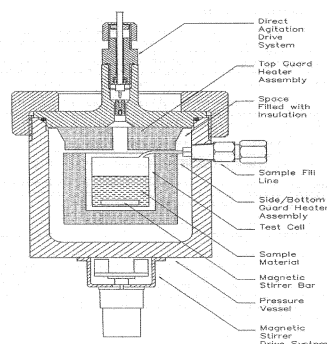

Figure 1: PHI-TEC II cross-sectional section.

Typical PHI-TEC II test mode is the *Heat-Wait-Search* (HWS) test. This test mode goes into a series of *heat* and *wait* step during which the sample is heated at different temperature and temperature stabilization is achieved. During the following search step self heating rate (SHR) of the sample mass is investigated. If SHR is higher than the set threshold (usually 0,02 °C/min) the calorimeter identifies the beginning of a thermal activity that is tracked in adiabatic mode. If no exothermic effect is found the calorimeter goes into a new HWS steps cycle. Adiabatic heat evolution is one of the worst incidental scenario for vent sizing, leading to wide relief areas.

3. Calculation model

To size a relief vent for a certain process normally we need to characterize the reagent mixture. To perform a system characterization in an experimental way three tests are needed (i.e. reactive system, flow type and flow regime characterization). On the other hand, using the batch-size approach, only one calorimetric test is required, leading to time and economical saving.

3.1 Reactive system characterization

Based on overpressure generation pathways, systems are divided in three types (Grolmes et al., 1989):

- Vapour systems: the overpressure is generated entirely by vapour pressure of the reagent mixture;
- Gassy systems: the overpressure is generated entirely by non-condensable gasses formation generated by the runaway reaction;
- Hybrid systems: these systems are in between a vapour and a gassy system.
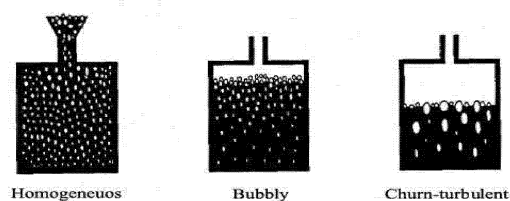
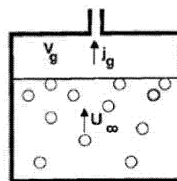**Figure 2: three flow regimes**   **Figure 3: reactor during a runaway**

Moreover the systems listed above can also be differentiated in tempered systems and non-tempered systems: in the first ones pressure is function of temperature, so pressure grows if temperature grows. In non-tempered systems there is no more this correlation.

Vapour systems are always temperate, instead of gassy systems are always non-temperate (Etchells and Wilday, 1998 and Fisher et al., 1992). Hybrid systems can be either temperate or non-temperate.

3.2 Regime flow characterization

Reagent mass can be characterized as foamy or non-foamy (Fauske, 2000). Foamy systems always relieve a two-phase mixture, this behaviour could also be caused by small impurities produced during the incidental scenario.

The flow regime can be divided into three categories (Grolmes, 1989): *homogeneous, bubbly, churn turbulent*. *Homogeneous systems* are characterized by no disengagement between gas and liquid phase, as consequence there is a great liquid swell. On the other side, in a *churn-turbulent system* there is a complete vapour-liquid disengagement and almost no reagent liquid mass swelling. A *bubbly system* has characteristics in between the previous two.

Homogeneous regimes are typical foamy systems, instead bubbly and churn-turbulent are correlated to non-foamy ones.

DIERS rule of thumb is that viscous systems (viscosity > 100 cP) generate a bubbly laminar flow regime, on the other hand low viscosity systems (viscosity < 100 cP) cause a churn-turbulent flow regime. In case of very high viscosity (viscosity > 500 cP) the flow will be homogenous and laminar.

3.3 Flow type characterization

When the venting takes place it can be classified in three categories:
- single-phase vapour flow: all the relief flow is gas or vapour
- single-phase liquid flow: all the relief flow is a liquid phase
- two-phase flow: the relief flow is a foam.

During an incidental scenario (e.g. a runaway reaction) solvent can evaporate or non-condensable gas can be generated. In these cases if every gas bubble in the liquid fills a bigger volume and the generated foam height is higher than the available void reactor space than a two-phase flow can occur.

Flow type characterization can be performed without experimental tests using analytical methods. The most important has been studied by DIERS. The operating procedure suggested by DIERS (Simpson, 1998) is:
- evaluate gas/vapour superficial velocity, j_g (Figure 3)
- estimate gas/vapour velocity while still entrapped in the liquid mixture, U_∞
- calculate liquid swell α

- compare α to void the fraction in the reactor α_0, to verify if single or two-phase flow occurs

j_g is correlated to liquid swell and generally rises with it. Moreover the volumetric flow W_{vol} is the sum of the non-condensable gas flow (Q_g) and vapour volumetric flow (Q_v):

$$W_{vol} = j_g \cdot A_R = Q_g + Q_v \tag{1}$$

Q_v can be calculated as:

$$Q_v = \frac{qm}{\Delta h_{ev} \rho_G} \tag{2}$$

Where q is the specific heat generated by the runaway reaction [kW/kg], m is the reagent mass [kg], Δh_{ev} is the latent evaporation heat [kJ/kg] and ρ_G is the vapour/gas density [kg/m3]. Q_g is evaluated with the following equation:

$$Q_g = \left[\frac{V_e}{P_R}\left(\frac{dP}{dt}\right)_R - \frac{V_e}{T_R}\left(\frac{dT}{dt}\right)_R \right] \frac{m}{m_e} \tag{3}$$

Where V is volume [m³], P is pressure [kPa], T is temperature [K], m is mass [kg] and the subscript *e* stands for the experimental test values and *R* for the values at the relief conditions.

Bubble rise velocity U_∞, is linked to physical properties and can be calculated as Levich (1961) suggests (Levich, 1961):

churn-turbulent flow regime: $\qquad U_\infty = 1.53(\sigma g(\rho_L - \rho_G))^{0.25} \rho_L^{-0.5}$ (4)

bubbly flow regime: $\qquad U_\infty = 1.18(\sigma g(\rho_L - \rho_G))^{0.25} \rho_L^{-0.5}$ (5)

where σ is gas-liquid surface tension [N/m].
Void fraction is function of the non-dimensional velocity Ψ which is calculated as:

$$\Psi = \frac{j_g}{U_\infty} \tag{6}$$

DIERS suggests the following equations in case of cylindrical reactors (Fauske, 1983 and Wallis, 1963):

churn-turbulent flow regime: $\qquad \alpha = \dfrac{\Psi}{2 + C_0 \Psi}$ (7)

bubbly flow regime: $\qquad \Psi = \dfrac{\alpha(1-\alpha)^2}{(1-\alpha^3)(1-C_0\alpha)}$ (8)

C_0 is a correlation parameter related to the type of studied system (D'Alessandro, 2004 part I and II).

4. Equations

In order to relieve a single phase flow from an ERS the following condition must be satisfied:

$$\alpha_{\text{SWELL LEVEL}} < \alpha_{VOID} \tag{9}$$

If the liquid swell is less than void fraction, a single phase gas/vapour flow occurs. Void fraction is calculated as:

$$\alpha_{VOID} = 1 - \frac{m/\rho_L}{V} \tag{10}$$

where m is the reactant mass [kg], ρ_L is the liquid density [kg/m^3] and V is the reactor volume [m^3].We can evaluate the total reagent mixture mass to be loaded in the reactor or the limiting reagent mass (i.e. making a dilution) in order to have a single-phase gas relief.

4.1 Evaluation of the total reagent mixture mass

The border conditions between single and two-phase relief can be evaluated making equal the void fraction and the liquid swell:

$$\alpha_{\text{VOID}} = \alpha_{\text{SWELL LEVEL}} \tag{11}$$

Considering equations (7) and (8) and that the correlation parameter C_0 is equal to 1 for foamy systems and equal to 1,5 for non-foamy systems, we can rewrite (11) for vapour system as:

foamy systems $\quad \psi\alpha^3 - \alpha^2 + \alpha - \psi = 0 \tag{12}$

non-foamy systems $\quad 1.2\psi\alpha^4 - (1+\psi)\alpha^3 + 2\alpha^2 - (1.2\psi+1)\alpha + \psi = 0 \tag{13}$

Solving equations (12) and (13) as a function of total mass m we can estimate the total reagent mixture mass.

4.2 Evaluation of the limiting reactant mass

We can evaluate the amount of the limiting reactant to be added in the reactor in order to have a single phase relief flow. Consequently the reagent mixture composition changes. In case there could be more than one limiting reactant the one used in the smaller amount or the one with best chemical properties will be chosen.

The first step is to calculate the void fraction α during an incidental scenario then, when the mass in the reactor is known, we can evaluate the mixture composition of the new reagent mass through an experimental calorimetric test.

Next step is the calculation of the non-dimensional bubble velocity Ψ as the ratio between the bubble velocity in the liquid U_∞ and the free bubble velocity j_g. Both these parameters need to be estimated. Then j_g is used to find the volumetric vapour/gas flows which are a function of the specific reactant mass.

For a vapour system the specific heat flow is used to correlate the volumetric flow and the limiting reactant mass.

The heat flow has been normalized by the massive fraction of the limiting reactant:

$$q = c_p \left. \frac{dT}{dt} \right|_{M,\phi} \tag{14}$$

Where c_P is the specific heat of the reagent mass (kJ/kg K) and $(dT/dt)_{M, \Phi}$ is the normalized self heating rate for the limiting reagent mass (K/s kg).

5. Incidental scenario and experimental tests

The choice of the correct incidental scenario is very important as this can deeply affect the calculation results. In this work we have considered as incidental scenario an external fire (calculating the fire heat flow as suggested by Parry, 1992, connected to the fill level), or a runaway reaction together with the failure of the cooling system (reaction runs adiabatically) and the possibility of foam generation in the reactor.

This approach can't be used to study gassy system because of the absence of tempering while ERS is relieving. For gassy system to simulate a fire exposure a second PHI-TEC II test is needed.

In order to show the results of the batch-size approach a vapour system is presented.

CASE STUDY: carbamate synthesis

The process is run in semi-batch way: mono-isopropyl amine (MIA) is dropped on dioxanone, at a temperature of 35°C to avoid MIA evaporation (T_{eb}=34°C).

To simulate a incidental scenario that can generate an overpressure and therefore a relief through the vent device, we run an adiabatic test with PHI-TEC II adding the MIA one-shot on the dioxanone starting from 35 °C. Figure 5 shows temperature and pressure behaviour of the reagent mass during time of the one-shot addition test.

If MIA addiction is too fast it evaporates therefore the system is a vapour system. This is testified also from Figure 4 where a behaviour similar to a vapour pressure system is followed by the system studied.
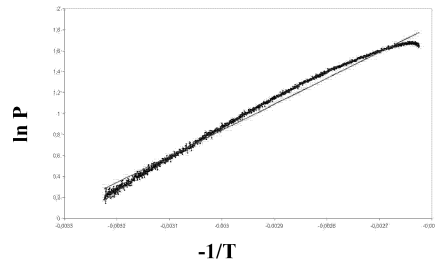
Figure 4: ln P vs –1/T for system type distinction
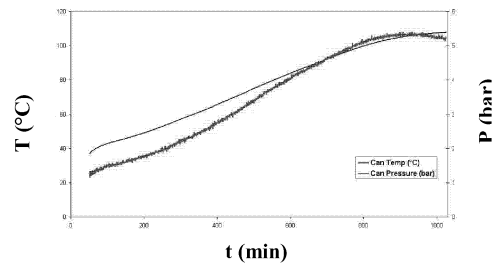
Figure 5: Temperature and pressure vs time of the MIA + dioxanone reaction

The adiabatic temperature rise and the heat flow are evaluated from the calorimetric test. Results are shown in Table 1.

Table 1: Adiabatic test results

dT/dt$_{MAX}$ [°C/s]	0.005
dT/dt$_{MAX}$ corrected for thermal inertia [°C/s]	0.006
q [kW/kg]	0.009

The calorimetric data obtained have been used to evaluate vent diameters for a set of reactors (i.e. five reactors with a volume of 3 m^3, 5 m^3, 7 m^3, 9.5 m^3 and 14 m^3) even though only the 7 m^3 reactor calculation will be shown in this paper (see Figure 6 and 7).

The explained method has been used to find the total mass values for each reactor, as shown in Figure 6 for the 7m^3 reactor where the total mass is presented as percentage of fill level.

The chosen limiting reactant is the dioxanone, in this way through the model we can define different areas for single and two phase flow. A fill level range between 50 and 99.5% has been investigated, as shown in Figure 7. Note as the hypothesis of external fire and foamy system is the worst scenario because the total mass to load in the reactor is less than for the others cases. Fire heat input leads to a big liquid swell: this is the reason why the reactor can be filled up just to 20%. Generally all the reactors have similar fill percentages, because they have the same geometrical features. The situation becomes more and more dangerous if the system is supposed to be foamy and an external fire occurs: the single phase flow area reduces and we have to use a smaller limiting reactant mass or a lower fill level. The results throughout the reactors in the total mass model and limiting reactant model are similar. Once that the incidental scenario and the chemical-physical properties of the reagent mixture are fixed there is a rise of the two phase flow area if the reactor volume increases.
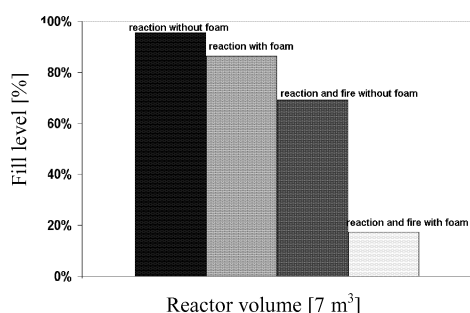
Figure 6: Fill level percentage of total mass vs reactor volume
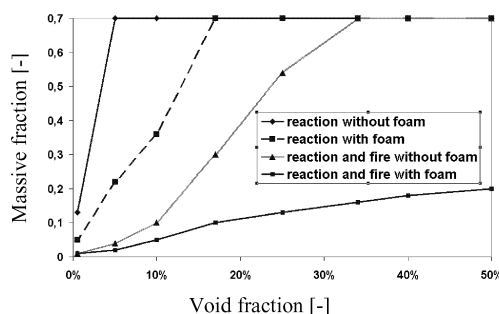
Figure 7: Limiting reactant mass ratio vs reagent void fraction for the 7 m^3 reactor

6. Conclusion

An alternative and cost effective approach to protect chemical reactors from overpressure has been investigated. Very simple variables, as mass or chemical composition, are used to define safety operative conditions. The maximum fill level has been calculated to avoid big liquid swell consequently a single phase flow occurs and the ERS installed can protect the equipment. After investigating accidental scenarios, total mass and limiting reactant mass fraction have been evaluated and presented in graphs. In these graphs boundary lines separate single phase from two phase flow areas. All the data needed for the evaluation can be obtained with just a single adiabatic

calorimeter test: this leads to big time and money saving giving a more competitive approach for SMEs.

7. Bibliography

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