Sizing Emergency Relief Systems for Multipurpose Plants

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Multipurpose reactors are very common in the specialty chemicals and pharmaceutical industries. Since these reactors often are designed to work under pressure, they must be equipped with an adequately sized emergency relief system (ERS). Due to the multipurpose character, the sizing of the ERS cannot be performed for a specific chemical reaction, but the design must be sufficient to cope with potentially very different reactions and different processing conditions. Hence it became a common practice to design the emergency pressure relief systems based on a credible physical scenario: in many cases, this is maximal heating applied on a volatile solvent. Maximum heating applied to a reactor results in very different flow behavior in the reactor compared to a chemical reaction, which results in a different mass flow rate to be discharged. The physical properties of a reaction mass may also be very different from a pure solvent as used in the design procedure, which results in a different discharge capacity. Thus the transfer of the design based on a physical scenario to a chemical scenario must be undertaken with care. A procedure allowing verification that the capacity developed for a physical scenario can be used for a chemical scenario and under which restrictions this transfer is valid was developed. The limitations are shown in the frame of a sensitivity analysis, allowing the identification of the critical parameters in the design. In every case, the behavior of a chemical reaction to be performed in a given reactor must be characterized with regard to its behavior under pressure relief conditions. This often involves an experimental study using different calorimetric techniques as adiabatic calorimetry, reaction calorimetry and Calvet calorimetry. Additionally, a simplified procedure based on past experience with the performance of the reaction at plant scale, but avoiding the calorimetric study is shown.

1. Introduction

1.1 Specificity of fine chemicals industries

In the present paper, the specialty chemicals, agrochemicals and pharmaceutical industries are subsumed in the denomination fine chemicals. The common characteristic in this industrial branch is the yearly amount of chemicals required, which are usually small compared to bulk chemicals. Thus, the syntheses are often performed in stirred tank reactors installed in multipurpose plants. These plants often present several dozens of reactors with different volumes, different material of construction and different peripheral equipment. Beside the diversity of the equipment, there is also diversity in the chemistry produced in one given reactor, e.g. the same equipment may serve for the production of over forty different products during one year. The production is organized in campaigns that may last from one week to several months. There is an additional constraint resulting from this type of production: the changes made on the equipment, when changing from one campaign to the next should be kept at a minimum. This particularly applies to the protection against overpressure, where the protection device, bursting disk or safety valve, should not be changed, when changing the production.

Consequently, the sizing of the emergency pressure relief system (ERS) should remain valid for different chemical reactions, or different physical situations. This requires a well-defined and traceable procedure, which is described hereafter. It became a common practice to use a two-step procedure for the design of the emergency pressure relief systems (Schmidt and Stoessel, 2011). The first step consists of sizing the ERS for a physical scenario; in a second step, this relief capacity is checked for a given chemical reaction. In a recent study, Schmidt presented example sizing calculations with a large panel of different solvents (Schmidt, 2011a, 2011b). He could show that in the frame of the scenario “external heating”, despite of the great diversity of the solvents, in most cases the required specific area expressed in mm²/kW remains in a relatively narrow range.
This gives a simple sizing method that requires the thermal power leading to pressure relief. These steps are described in the following sections.

1.2 ERS sizing using a physical scenario
In a first step, the sizing itself is performed based on a credible physical scenario. In many cases, this is maximal heating applied on a volatile solvent. In this scenario, a failure of the temperature control system is assumed, which results in the application of the full heating capacity to the reactor. The reactor is supposed to contain a solvent, which is heated leading to a pressure increase according to its vapor pressure. Thus the nature of the solvent has a great influence on the ERS sizing. The sizing calculation is performed in compliance with the standard ISO 4126-10 (ISO 4126-10, 2010). It results in a given discharge capacity determined for the physical scenario, and thus, the question arises how far this capacity can be used for a chemical system. There are three types of parameters entering into the sizing calculation:
- operating parameters as the degree of filling of the reactor, the set pressure of the ERS
- the nature of the solvent used for sizing calculations and its physical properties as the vapor pressure, the density, the surface tension, the latent heat of evaporation, the heat capacity
- technical data of the reactor as its diameter and its overall heat exchange area, the temperature of the heat carrier, the geometry of the relief system.
Hence the variability is large, which requires certain choices to be made. Showing the effect of the design parameters on the result of the vent sizing calculation is one of the objectives of the present paper.

1.3 Checking the available relief capacity for a given chemical reaction
In the second step of the procedure, the installed capacity must be checked for a given chemical reaction that has to be performed in the reactor. The question is to assess how far this capacity can be used for a chemical system.

Maximum heating applied to a reactor results in very different flow behavior in the reactor compared to a chemical reaction: this is essentially due to the fact that with a chemical reaction the vapor bubbles are formed homogeneously in the bulk of the reaction mass With external heating, the bubbles of vapor are formed at the reactor wall, resulting a higher in a different flow pattern than with a chemical reaction. With chemical reactions it is recommended to use a homogeneous flow model, whereas for external heating a churn flow model would allow for a better description of the flow pattern.

These different flow patterns in the reaction mass will also induce different flow patterns during pressure relief. The consequence may be that the mass flow rates to be discharged are affected. The physical properties of a reaction mass may also be very different from a pure solvent as used in the design procedure, which results in a different discharge capacity. Thus the transfer of the design based on a physical scenario to a chemical scenario must be undertaken with care, as is shown in the present paper.

1.4 The example process
An exothermal chemical reaction has to be performed as a semi-batch reaction in a stainless steel 4 m³ reactor with a total reaction mass of 3400 kg at a temperature of 45 °C. The solvent is methanol and the vapor pressure of the system is essentially that of methanol. There is no gas release during the reaction. A calorimetric study of the reaction performed under normal operating conditions shows that the maximum accumulation corresponds to an adiabatic temperature rise of 70 K. The heat release rate at the instant of maximum accumulation is 20 W/kg. If a cooling failure occurs at this instant, the temperature and accordingly the pressure will rise.

The reactor is protected with a safety valve at an absolute set pressure of 4 bar. The dimensionless discharge coefficients are 0.67 for a gas and 0.45 for a liquid. The maximum accumulated pressure during relief must not surpass 4.3 bar and the back pressure is atmospheric. The maximum volume before flooding is 5.525 m³. The overall heat transfer coefficient is assumed to be 1000 W/(m²K) and the heat exchange area is 7.4 m². The maximum heating medium temperature is 150 °C. The sizing calculation for the scenario “external heating” is performed with 4 m³ of methanol at 25 °C, i.e. 3144 kg.

2. Sizing for maximum heating
The procedure essentially follows the five steps from the ISO 4126-10 standard:
1. Definition of the design case
2. Determination of the nature of flow
3. Determination of the mass flow rate to be discharged
4. Determination of the required relief area
5. Checking the valve stability (this step is not treated in the present paper).
Using the vapor pressure of methanol, the temperature at the set pressure of the safety valve, 4 bar, is 104 °C (at maximum accumulated pressure it is 106 °C). The heat input to the vessel, 340 kW, is calculated using the overall heat transfer coefficient 1000 W/(m²·K), which is relatively high but representative for heat exchange with evaporation. The heat exchange area also varies with the degree of filling. Often, in order to provide a systematics, the reactor is considered to be filled with the solvent at its nominal volume at room temperature. This allows standardizing the degree of filling. Nevertheless, the degree of filling under relief conditions will vary from one solvent to another since the boiling points and the volume expansion factors are different.

The assessment of the nature of flow one or two phase flow, is done following the DIERS methodology (Fisher et al., 1992) using the bubble rise velocity. This bubble rise velocity is then compared with the limit bubble rise velocity for churn turbulent and bubbly flow (Figure 1). In the present case, one phase flow may be expected for the churn turbulent model, but two phase flow must be expected for the bubbly flow model.

The mass flow rate to be discharged, 11.2 kg/s, is determined using the Leung’s method for tempered systems (Leung, 1996). The dischargeable mass flux is calculated using the Omega model (Leung, 1996), by calculating the critical pressure ratio and then the mass flux: 3463 kg/(m²·s). The required discharge area, 53 cm² is calculated by dividing the mass flow rate to be discharged by the dischargeable mass flux corrected by a discharge coefficient (0.61), obtained as a weighted average from the coefficients for gas and liquid phases. In a safety valve nozzle the thermodynamic equilibrium may not be reached, resulting in a boiling delay. To account for this, a non-equilibrium model was developed by (Diener and Schmidt, 2004) introducing a correction factor for the calculation of the compressibility. Taking this factor into account, the dischargeable mass flux is increased to 5896 kg/(m²·s), which represents an increase of the discharge capacity by 33 % for the present case. Then the required nozzle is 35 cm². Thus a Safety valve with a nozzle diameter of 72 mm will be installed. The corresponding thermal power is ca. 400 kW or 127 kW/kg.

This size was calculated for methanol, but the reactor may also be used for other solvents. Calculating a relief capacity requires to gather and generate a large set of data. Not all of them can be determined with high accuracy. A sensitivity analysis will show which require most attention.

3. Parametric sensitivity

3.1 Effect of the solvent

Different common solvents: methanol (MeOH) as base case, acetone, dichloromethane (CH₂Cl₂), ethanol (EtOH), water (H₂O), Tetrahydrofuran (THF) and toluene were used in this study in order to define which type of solvent may be most critical with respect to the required relief area (Figure 2). In all cases, the volume at relief was the same: 4 m³. With toluene, the vapour pressure at 150 °C, the maximum heating medium temperature is lower than the set pressure.
It becomes obvious that dichloromethane is the solvent, which requires the largest relief capacity. This is essentially due to two reasons: the comparatively low latent heat of evaporation and the low boiling point, leading to a high heat input under relief conditions.

### 3.2 Effect of the physical properties

Physical properties are often known with only poor accuracy. For this reason, the most important physical properties (latent heat of evaporation, vapor pressure ($P_{set}$ and $P_{max}$ reached at temperatures different than foreseen), the density, the latent heat of evaporation, the heat capacity) were varied in the methanol case (departing from reality). The latent heat of evaporation has a significant effect on the relief capacity while the remaining parameters only have a slight impact as seen in Figure 3. The influence of changes in the vapor pressure, hence the temperature at relief, influences the relief area but also influences the heat input at relief and hence overall, the specific relief area only slightly varies.

### 3.3 Effect of the technical parameters

The technical parameters (volume resp. degree of filling, set pressure and maximum pressure) were varied similarly to the physical parameters (Figure 3). Changing the set pressure had a significant effect, while the other parameters had only a small effect. Indeed, a variation of the relief pressure also modifies the temperature at relief and hence the heat input due to maximal heating. This analysis shows how essential it is to choose the appropriate relief pressure for a given relief operation.

The heat transfer coefficient is most of the time also estimated. In the present case its variation will change the relief area linearly and therefore not influence the specific relief area.
4. Evaluation of the capacity for a chemical reaction

4.1 Behavior under relief conditions
The present case is treated as a tempered system, thus the temperature rise from process conditions to the set pressure is 59 K, which represents a conversion of 84 % of the accumulated reactant. The heat release rate under relief conditions can be determined by different ways.

Ideally the reaction is performed in an adiabatic calorimeter, preferably with a low thermal inertia (e.g. Fauske VSP2 or similar instruments) providing a direct determination of the temperature and pressure increase rates. This allows a direct calculation of the heat release rate of the reaction that is used for the sizing calculation.

A further possibility is to study the reaction kinetics in a Calvet calorimeter (e.g. Setaram™ C80) that allows the simultaneous measurement of the heat release rate and of the pressure increase rate under strict temperature control. Performing different experiments at different heating rates allow applying an isoperibolic method for the kinetic evaluation, which in turn is used for numerical simulation of the adiabatic behaviour (Roduit et al., 2004).

4.2 Sizing without calorimetric experiments
When no experiments are available one can still proceed via estimation using the Van’t Hoff rule (reaction rate doubles or triples for a temperature increase of 10°C). The heat release rate may be extrapolated from 45 °C to 104 – 106 °C, which gives 1194 resp. 1372 W/kg at the set resp. maximum accumulated pressure. This calculation only considers the acceleration of the reaction according to Arrhenius law. But at the same time, during the temperature rise from 45 to 104 °C, some conversion takes place, this reduces the reaction rate. Thus an acceleration phase followed by a slowing down of the reaction results. Assuming a fist order reaction (conservative), the remaining accumulation at 104 °C is 16 %. Thus the power of the reaction is reduced to approximately 188 W/kg. Taking tripling the reaction rate for a temperature increase by 10 K, the resulting power would be above 2000 W/kg. These values are too high for the installed emergency pressure relief system, which allows 127 W/kg. Another approach is possible when experience on performing the reaction at plant scale is available. The power of the reaction can be estimated from the cooling capacity required to maintain isothermal conditions. Thus knowing the maximum allowable power under relief conditions, in the example 400 kW, the maximum allowable power under process conditions can be extrapolated by making an assumption on the activation energy (e.g. 100 kJ/mol). Figure 4 shows the extrapolation for our case with different accumulated energies. The allowable power under process conditions is expressed as a minimum allowable cooling medium temperature: if at plant scale the cooling temperature is below this value, then the installed relief capacity is too small. This pragmatic approach strongly depends on the assumed activation energy.

![Figure 4: Minimum allowable cooling medium temperature as a function of the process temperature and accumulated energy ($\Delta T_{ad}$)](image)

4.3 Effect of the choice of the solvent
In a multipurpose plant, it may happen that a reaction is performed using a different solvent from that was used for sizing purpose. In this case neither the temperature at the set pressure nor other physical properties correspond to the sizing parameter. This effect is shown using a reaction with a power of 20 W/kg at the process temperature of 45 °C. The power under relief conditions is calculated and compared to the power corresponding to the discharge capacity (Figure 5). In this example only sizing with the “most critical” solvent, i.e. dichloromethane allows for a sufficient discharging capacity. Nevertheless it must also be considered that for ethanol, water and THF no relief occurs at all, since the temperature increase does not allow triggering the
pressure relief. These are also safe situations, and even closer to inherent safety than the discharge cases.

<table>
<thead>
<tr>
<th>Reaction power</th>
<th>MeOH</th>
<th>Acetone</th>
<th>CH₂Cl₂</th>
<th>EtOH</th>
<th>H₂O</th>
<th>THF</th>
</tr>
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<tbody>
<tr>
<td>kW</td>
<td>440</td>
<td>457</td>
<td>434</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<table>
<thead>
<tr>
<th>Installed power</th>
</tr>
</thead>
<tbody>
<tr>
<td>435</td>
</tr>
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Relief system not triggered

Figure 5: Comparison of the thermal power corresponding to the sizing with the power required by a chemical reaction. Dark grey: installed capacity to low; bright grey Installed capacity sufficient

4.4 Problem solution
In the present case, rather than increasing the discharge capacity, the solution of the problem is clearly a process change that reduces the accumulation. If the adiabatic temperature rise due to accumulation is reduced from 70 to 59 K, the pressure relief system would not been triggered during the runaway. This also shows that the process design is important and a wrong design may lead to costly solutions if pressure relief is required. The investment linked to a pressure relief system is not limited to the solely pressure relief valve, but the effluent treatment if it has to cope with high discharge rates, may lead to high costs.

5. Conclusions
As seen from the parametric sensitivity analysis, the heat of evaporation has to be determined with care. A possibility is to determine it experimentally from a pressure temperature curve (for example with Calvet Calorimetry) using the Clausius-Clapeyron equation. Such an experiment can also be used to verify the pressure and temperature at relief. Similarly, choosing the appropriate pressure at which the pressure relief system is triggered is essential as it greatly affects the relief temperature and capacity. The thermal power at relief conditions is the determining factor as well for sizing as for checking the compatibility of a reaction. The allowable thermal power is determined for the relief temperature, which changes for different solvents due to their different volatilities. Higher volatilities lead to higher allowable power at relief under process conditions.

Since the power of a reaction exponentially varies with temperature, values based on estimations may lead to considerable errors. The example used in this paper shows that a chemical reaction, even if apparently harmless at process temperature (20 W/kg), may give rise to considerable power under relief conditions (ca. 200 or even above 2000 W/kg). Thus it is important to base the sizing calculation on a strong experimental set.

References