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Protection of Chemical Reactors Against Exothermal Runaway Reactions with Smart Overpressure Protection Devices

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Mechanical safety devices and safety integrity systems are widely spread in the industry to protect chemical reactors against runaway reactions. However, these devices are limiting the productivity and flexibility of the plants due to their fixed set conditions and discharge areas. Hence, a new, intelligent, and adaptive safety device is required in the industry. This article presents a structure containing three modules for the new safety device. For each module, a detailed evaluation of available methods and devices to meet the requirements of reliability, flexibility, and precise countermeasures for the safety device have been performed. Concluding, a basic structure of the adaptive safety devices is outlined. The article summarizes research results submitted for publication in (Schmidt, 2022).

1. Introduction

Chemical reactors in batch- and semi-batch operation mode are widely used in the industry to produce a huge variety of primary- and special chemicals. Uncontrolled reactions can lead to exponential sudden heat release followed by an abrupt temperature and pressure increase, a so-called “runaway reaction”. A runaway reaction can cause impermissible reactor conditions, often this scenario is the worst-case scenario for sizing safety devices. There are multiple possible scenarios leading to runaway reactions, e.g., loss of cooling, stirrer failure, wrong dosage, or missing catalyst. To protect the reactor from exceeding the design limits, mechanical safety devices for pressure relief and high integrity programmable logic control systems (HPLC) are applied in the industry. Both types of safety devices have in common that predefined shutdown limits are usually set conservatively low to avoid an uncontrolled runaway reaction. The standard TRAS410 gives an example of these limitations (BMAS, 2012), where it is recommended to set the shutdown limit for exothermic reactions conservatively 100 K below the reaction onset temperature. Consequently, according to Arrhenius law, these limitations reduce the plant’s productivity with increasing energy release at higher temperatures. Thus, safety criteria like the divergence criterion by Hub and Jones (1986) and further developed by Zaldívar et al. (2003), the adiabatic criterion of Guo et al. (2017), or the accumulation criterion from Deerberg (1995) implemented as energy balance method by Schmidt and Giesbrecht (1998) have been published over the last decades. However, the criteria are rarely used due to uncertainties, sensitivities, or their low prior alert time, according to Biernath et al. (2021).

Regarding multi-purpose plants, optimum protection for each reactor cannot always be provided by only one type of safety device. For highly exothermic and fast reactions, sticking, or corrosive materials, HPLC protection is in some cases more applicable than a mechanical safety device. The type of device strongly depends on the reaction components and the process conditions. In addition, a review of the conventional safety devices (e.g., setpoint or dimensioning) must be carried out whenever safety-relevant changes are applied to the plant or the process conditions. The result reduces flexibility for a quick recipe and process changes as generally required in multipurpose plants. Thus, the demand for a new safety device in the industry to increase efficiency and flexibility under the assurance of the highest safety standards for the plant needs to be fulfilled.

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2. The concept of an adaptable safety device

Nowadays, mechanical safety devices and safety integrity systems are generally designed to the worst-case scenario for their desired process and recipe. The worst-case condition usually occurs only in a short period during the reaction. But all other process conditions and recipes are limited regarding production and flexibility due to the fixed shutdown limits. Therefore, the safety concepts of chemical reactors should change from an overall worst-case recipe, process, and plant-based protection to a current online performed analysis depending on the reaction progress and the reactor design limits. The future should be not to size a suitable safety device depending on the design limits of the reactor, the reaction mode, and the plant configuration, but to use an adaptive safety device directly connected with the reactor, which performs a current evaluation of the safety condition of the reactor over time, based on actual plant and recipe parameters. Subsequently, this evaluation must then ensure the initiation of adequate countermeasures in the event of critical plant conditions. Thus, a safety device is required that can perform such an evaluation without exceeding the plant limits. To find such a safety device, it is at first necessary to define the requirements for the concept of an adaptable safety device:

- **Adaptable to processes and plants:** For different chemical reactions, process type and plant designs, e.g., batch, semi-batch, multipurpose plants, the adaptable safety device needs to be recipe, process, and equipment adaptable.
- **Reliable detection of runaway reactions:** The adaptable safety device needs to detect occurring runaway reactions reliably and initiate appropriate countermeasures. The reliability of mechanical safety devices is usually guaranteed by a type test and subsequent approval as a safety device according to ISO 4126 (DIN E. V., 2016). For electrical, electronic, or programmable electronic safety-related systems, the safety integrity level is used as a measure of reliability. To ensure safety functions of chemical plants with high risks, a SIL-Level of 3 is often required for the whole SIS system, including logic controller, sensors, or other electronic supported systems and actuators as shown by DIN 61508 (DIN E. V., 2011). For widespread use in the industry, a new, adaptable safety device needs to fulfill the requirements of a SIL 3-level as well.
- **Evaluate risk potential and initiate countermeasures:** The adaptable safety device must evaluate the risk potential continuously and initiate specific countermeasures if the risk exceeds a given threshold. Appropriate countermeasures depend on the chemical reaction, process, and recipes, and ensure the plant's safety. They must be applied within a maximum response time. Uncertainties regarding sensors, models, and actuator setting accuracies must be accounted for.

To meet the requirements outlined above, the new, adaptable safety device requires a three-stage structure to detect the hazards, determine the hazard potential for the plant, and initiate adequate countermeasures. The three modules are outlined below:

Module 1: Runaway detection method

All parameters belonging to specific recipes, processes and reactor design must be safely deposited into the HPLC of the new, adaptable safety device and validated. Appropriate safety related input interfaces are needed. A method for precise and early detection of a runaways for the variety of chemical reaction and process types must be implemented. A sufficient response time to automatically initiate countermeasures must be guaranteed.

Module 2: Risk potential assessment methodology

The design limits of the reactor shall not be exceeded. A precise methodology to reliably evaluate the actual risk potential for a specific production is required. At each moment of the production, possible deviations from normal plant operation or a drift of parameter out of the normal production range must be estimated and evaluated. It is desirable to estimate the risk potential continuously, at any time during the reaction process.

Module 3: Countermeasure evaluation system

The adaptable safety device must include an evaluation system to determine and initiate adequate countermeasures depending on the hazard potential of a reaction, the process type, and the design limits of a reactor. Countermeasures may either redirect the process into normal operation or at least to permissible conditions (e.g., feed stop, cooling activation, reaction inhibitors injection, etc.), or initiate a pressure relief.

In the following, models and approaches from literature and industry suitable for the three modules are being reviewed to meet the requirements for the adaptable safety device specified above.

3. Approaches for the three modules of the adaptable safety device

In the following, methods and models matching the three modules presented above are being reviewed and evaluated against the requirements for the adaptable safety device.

3.1 Module 1: Runaway detection method

A literature review on runaway criteria for a potential use in the adaptable safety device has been performed. Further methods such as artificial neural networks or expert systems have been evaluated but are not the focus of this summary.

Hub and Jones (1986) developed one of the first empirical approaches for online safety criteria without using complex kinetic data or fluid properties, the origin of the divergence criterion. The results were two expressions, based on the second derivative of the reactor temperature over time t and the difference between the reactor T_R and cooling temperature T_c, indicating a possible runaway reaction when both show a positive value. Studies on the runaway criterion from Hub et al. have shown amplification of measurement fluctuation caused by the second derivation of the temperature (Strozzi et al., 1999). Further development of the proposed criterion has been done by Zaldívar et al. (2003), who extended the number of parameters considered in the divergence criterion, Eq (1).

$$div[F(\theta, X_A, X_B \dots)] = \frac{\partial F}{d\theta} + \frac{\partial F}{dX_A} + \frac{\partial F}{dX_B} + \cdots > 0 \tag{1}$$

θ, X_A and X_B are state variables which are basically partial derivatives of the mass and energy balance of the reactor. The state variable θ consists only of the reactor temperature, the conversion rates X_A and X_B are depending on the concentrations of the components A and B. Thus, the reaction progress can be monitored, and a positive divergence caused by an unwanted accumulation inside the reactor will indicate a runaway reaction. Biernath et al. (2021) has shown, using the divergence criterion with standard temperature sensors, that detection of the runaway is only possible shortly before the adiabatic end temperature is reached and thus shortly before the end of the runaway reaction. An alarm threshold needed to be set up to a high and insensitive value to avoid false alarms. Possible countermeasures could thus be initiated too late. Summarizing, the divergence criterion can be used in specific reactions as a supporting warning system to identify runaway reactions early. Still, due to the amplification of measurement noises, the usage in a safety-related device may result in several false alarms. Reliable detection of runaway reactions can thus hardly be achieved.

Guo et al. (2017) published an adiabatic criterion to indicate runaway reactions based on kinetic data and adiabatic temperature increase for a homogeneous and heterogeneous liquid-liquid reaction. Guo et al. (2017) state if the first derivative to time of the heat released by the reaction is always negative (<0), the reaction temperature can be adequately controlled during the reaction process. The results show a more conservative behavior of the adiabatic criterion than the divergence criterion because the adiabatic criterion is more likely to detect critical situations than the divergence criterion. This also increases the probability of false alarms, shown by Biernath et al. (2021), for liquid-liquid reactions with an accumulation of the reactants during normal process operation mode. Besides, it becomes apparent that the adiabatic runaway criterion proposed by Guo et al. (2017) requires the knowledge of the kinetic data of the reaction (such as the reaction orders or activation energies), which are often imprecise and strongly depending on the temperature range and the purity of the materials. Hence, kinetic data are rarely used in safety-related functions by referring to the reliability requirement for the adaptable safety device.

3.2 Module 2: Risk potential assessment methodology

The risk potential of exothermic chemical reaction depends on the concentration of reactive substances accumulate at a certain instance in a reactor. Hence, an assessment methodology must consist of a model to calculate the accumulated mass of reactant $m_{ac,c}$ at any timestep. Herewith, the maximum temperatures and pressures at an instantaneous conversion of the accumulated mass can be calculated (Steensma and Westerterp, 1990). If the calculated, maximum temperature of a potential runaway may exceed the safety threshold of the reactor, countermeasures, e.g., a feed stop can be initiated. Many of the approaches for the accumulation criterion are based on an adiabatic temperature rise caused by an instantaneous conversion of huge reaction masses. The maximum adiabatic Temperature T_{ad} to be reached from starting temperature T_0 can be calculated by Eq (2):

$$T_{ad} = T_0 + \frac{-\Delta H_R(T_R) \cdot c_{acc}}{\rho_R \cdot c_{p,L}} = T_0 + \frac{-\Delta H_R(T_R) \cdot m_{acc}}{\rho_R \cdot c_{p,R} \cdot V_R \cdot M_{acc}} \tag{2}$$

The calculation is based on the temperature dependent heat of reaction ΔH_R, the accumulated concentration of the reference component c_{acc}, the density of the reactor content ρ_R and the specific heat capacity of the liquid $c_{p,L}$. The accumulated concentration can be directly converted to the accumulated mass by taking the molar mass m_{acc} and the reactor Volume V_R into account. To obtain the accumulated mass, direct measurements or calculation approaches as the energy balance approach can be used.

The energy balance approach (ENB) is a well-known method in the literature (Schimetzek and Giesbrecht, 1999), (Deerberg, 1995) to calculate online the accumulation of the reactant inside semi-batch reactors based on an extensive energy balance similar to the adiabatic criterion. The accumulated mass can be calculated from the difference between the ingoing and outgoing energy transfer (Eq. (3)). The integral form of the ENB approach is presented below.

$$\int_0^t m_{acc} dt = \frac{\int_0^t m_{in} \Delta H_R dt - \int_0^t Q_R dt}{\Delta H_R} \tag{3}$$

Q_R is the integrated energy released by the reaction, which can be tracked by integrating all other measurable energy inputs over time. m_{in} is the fed mass of the reactant. No kinetic information about the reaction is required here. Biernath et al. (2021) stated that due to integrating the energies over time, a high sensitivity caused by the inevitable integration of measurement uncertainties is expected. High uncertainties and large safety margins are the result.

Compared to the requirements for the adaptable safety device, an accumulation criterion can monitor the accumulated mass over time and, therefore, detect critical situations before the runaway even starts. Thus, the potential to initiate countermeasures in time, and to bring the process back to a safe condition, is high. Also, implementing SIL3 capable systems is possible. Involved electrical components such as sensors, logic units, and actuators are available sufficiently. Hence, the accumulation criterion fulfills the required reliability. It can be defined recipe and plant independent to increase the flexibility of the methodology. Nevertheless, the safety margins must be adapted to the respective process. To reliably obtain the accumulated mass despite of the integration of measurement uncertainties, further research to improve the accuracy of accumulation criteria or to develop an accumulation criterion based on different measurement values to decrease safety margins needs to be performed.

3.3 Module 3: Countermeasure evaluation system

The two most common ways in industry to protect the reactor after a thermal runaway reaction has already started are pressure relief devices (PRD) and safety instrumented systems (SIS). Both protection device methods are being reviewed regarding the requirements for the adaptable safety device.

The SIS safety devices protect the system with the help of high integrity programmable logic controllers (HPLC), sensors, and actuators. Suppose the process exceeds the pre-defined limits (Pressure, Temperature, Level, Flow, etc.), the controller sends signals to the actuators to bring the process back to the predefined conditions or shuts the whole process in a fail-safe condition. A methodology for risk assessment, a model for detecting a runaway, and an evaluation system may consist of several hundred mathematical equations to be implemented in the HPLC. A sufficient performance and reliability are mandatory. For the decision of reliability, and therefore, the level of safety integrity (SIL-Level), a SIL-allocation considering the severity and likelihood of the protected failure scenario needs to be performed. A high severity is likely to be expected for exothermic reactions, leading to a SIL-Level of 3. Hence, according to IEC 61508 (DIN E. V., 2011), independent third parties must review the signal processing chain and the software architecture. Countermeasures appropriate for almost any scenario (e.g., feed stop, dumping, increased cooling), and the automation control is state of technology. An evaluation system may be developed from these experiences but is not yet available in the literature.

Overall, SIS usage for module 3 of the adaptable safety device approach is promising. Reliable processing chains can be obtained to the highest safety integrity levels (SIL), containing sensors, logical processing units, and actuators. Especially for highly exothermic reactions it will most likely not be possible to limit the pressure and temperature at all reaction stages below the design limits by SIS systems. A hybrid adaptable safety device could be beneficial.

Pressure relief devices (PRD´s) are widely spread in the industry due to their reliability and cost-effectiveness. Typical PRD´s are safety valves or rupture discs. After reaching their set pressure, PRD´s discharge a certain amount of the reaction mass through a vent line into the environment or downstream facilities. The main advantage of safety valves towards rupture discs is their ability to reclose which prevents most of the contents of the reactor from being discharged. The industry appreciates the functionality and simple design of a safety valve. But it still has some disadvantages which are hard to overcome.

- **Inflexible**: The static set pressure and fixed lift of a safety valve installed, e.g., in a multipurpose plant limit the processes. Changes in the recipe always require a new safety analysis and often adapt the process conditions to the installed safety device. Changing the set pressure or the lift height would require disassembling the valve and examining the correct valve function. Thus, the effort to design a safety device for different products is relatively large (Schmidt, 2011).

- **Valve chattering:** The spring-mass-damping system of the valve in combination with acoustic and pressure waves moving through the connected piping and getting reflected by the reactor and the connecting inlet- and outlet pipes can lead to high-frequency opening and closing of the valve. The phenomenon is called valve chattering or fluttering, and the causes are not yet sufficiently understood. Different literature suggestions have been presented by Frommann and Friedel (1998), a final solution is not yet found Darby (2013). It often goes along with potentially damaging the valve itself or the connected pipe, and the discharge capacity of the valve cannot be reached. A loss of the safety function is a possible impact.

- **Dynamically changing of dischargeable mass flow rate:** Downstream equipment such as liquid separators, quenches, or flares all work best at their intended operating point, defined mainly by the designed mass flow. As the mechanical safety device fully opens, the pressure in the protected system decreases, and therefore, the discharged mass flow is reduced. Continuing, the composition of the mass flow is also changing by time (Schmidt and Giesbrecht, 2001). Thus, during the emergency relief, the operating point of the downstream equipment is frequently missed, leading to pollution of the environment.

To summarize, all currently available safety devices are unsuitable for an adaptive safety system without restrictions. Further research is required to develop a SIL3-capable device that is at the same time process adaptable in terms of set pressure and discharge area.

4. Smart overpressure protection device (SmOP)

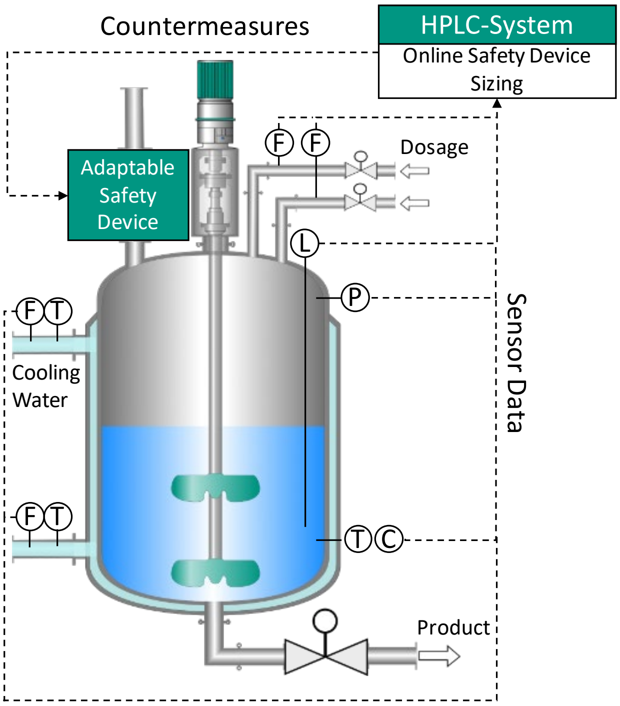

Figure 1: Outline of the SmOP-concept

The new adaptive safety device shall consist of the three modules to fulfill the former defined requirements and is called **Sm**art **O**verpressure **P**rotection Device (SmOP). The framework is described based on Figure 1.

The key of the concept is the HPLC safety device, which can control an adaptable safety device installed in the vent line of the pressurized system. To fulfill the requirements for module 1, the safety device should be adjustable in set pressure and discharge area, allowing widespread application combined with a controlled discharge procedure. A suitable device that can be controlled by an SIS system is unavailable and needs to be developed. The HPLC safety device, in combination with SIL3 capable process sensors such as temperature, mass flow, and filling level, should provide the necessary reliability for all electrical, electronic, and programmable devices. A programmed model in the HPLC device shall be used to control the set pressure and the relief cross-section area by calculating the risk potential inside the chemical reactor according to the chosen process and reaction, used as step 2 of the concept. An accumulation criterion is a promising approach. Available models like the ENB-approach suffer from uncertainties, as Biernath et al. (2021) has shown. Complex mathematical operations usually cannot be performed in an HPLC device. Therefore, a simple, kinetic-free model should be used to provide adequate countermeasures. In case of a runaway reaction, the model should first predict if the design limits of the reactor can be exceeded. In that case, countermeasures like a feed stop or the increase of cooling can be used to prevent undesired reactor conditions. To increase the allowable accumulated mass of educts in the reactor and thus reduce the batch time, a “controlled-emission”-mode can predict the optimum relief conditions (time and pressure) and the necessary relief area of the adaptable safety device. In addition, early detection of the upcoming runaway reaction is required to trigger the initiation of countermeasures. To fulfill the requirements of module 1, the kinetic free divergence criterion is currently the most promising early detection approach. A prototype is under development at CSE Center of Safety Excellence. Further research on the thresholds and the sensitivity of the divergence criteria is necessary.

Nomenclature

$c_{p,R}$ – reactor liquid specific heat capacity, J/kgK
m_{acc} – accumulated mass, kg
m_{in} – total added mass, kg
M_{acc} – molar mass accumulation, g/mol
Q_R – released reaction energy, J
t – time, s
T_{ad} – maximum adiabatic temperature, K
T_c – cooling temperature, K
T_R – reactor temperature, K
T_0 – starting temperature, K
V_R – volume reactor, m³
X_B – conversion component B, -
θ – state variable, -
ρ_R – reactor liquid density, kg/m³
ΔH_R – heat of reaction, J/kg

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