

## Design of Pressure Relief Devices for Chemical Reactors on the Basis of Adiabatic Tests – Is this always Conservative?

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Is the assumption correct that closed adiabatic tests for the design of pressure relief devices are always conservative? This issue will be investigated in different reaction systems. An effect is postulated, according to which higher temperature rise rates can be reached in adiabatic pressure relief tests in comparison to those in closed adiabatic laboratory tests. This effect can be described as a “distillation effect”. To describe the distillation effect we developed a theoretical number containing the essential characteristics with respect to the energy production by a runaway system and the energy dissipated by the evaporation of solvent during the pressure relief. To investigate the effect, two different reaction systems were examined. Initially, these systems were modified based on predefined criteria.

The distillation effect could not be identified by the experimental studies. In principle, the effect is expected when the reaction system has certain properties. Herewith, the reaction must have a high reaction energy and the solvent must have the highest vapor pressure in the system. Furthermore, the reaction heat must be high enough to evaporate the whole solvent and there must be enough energy to accelerate the heating of the reaction system. Overall, it was shown that the effect can be expected only in very few reaction systems.

### 1. Introduction

The design of pressure relief devices (safety valves or rupture discs) for chemical reactors requires knowledge of heat and gas production rates for the failure scenario considered. The reaction characteristics are generally determined in experiments using adiabatic calorimetry to allow for transferability of the experimental results to the conditions of the production reactor without additional correction factors. These tests are usually carried out in closed test vessels. Extrapolating from milliliter to cubic meter scale can be particularly challenging if conditions in the production reactor are not suitable in comparison to a closed vessel.

Differing conditions could be reached when a failure-related pressure and temperature rise in the reactor activates a pressure relief device. A portion of the solvent would evaporate off the reaction mixture and be removed via a vent pipe. In some reactions, this effect can lead to higher temperature rise rates than expected in a closed system. Figure 1 shows this effect. First, the courses of the closed test cell experiment and an experiment with a pressure relief device representing a batch reactor with a safety valve have the same temperature rise rates up to the set pressure of the safety valve (see Figure 1). At this point, where the pressure relief begins, a difference between the two temperature rise rates becomes apparent. While the temperature rise rate of the closed test cell experiment increases approximately linearly, the experiment with a pressure relief decreases at first, due to the cooling effect of the evaporating solvent which discharges through the safety valve. Due to the evaporating solvent, an increasing concentration of the reactants or catalyst in the reaction system may occur and consequently higher temperature rise rates can be reached after the evaporation. This process can be described as a “distillation effect”, because by distilling off the solvent, boundary conditions of the reaction system will be changed. Thus, it might be possible that the heat or gas generation rates, determined under adiabatic conditions in a closed test cell, are not conservative anymore. Such an underestimation of the temperature rise rate could lead to wrong dimensioning of the pressure relief

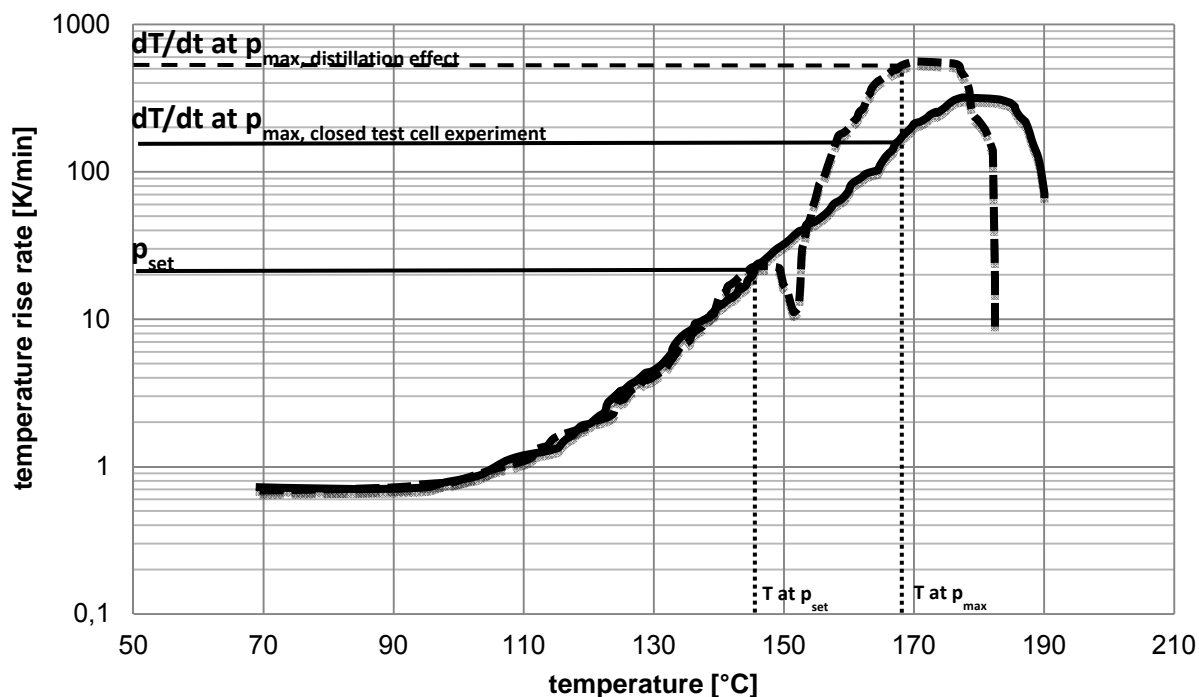


Figure 1: Representation of the temperature rise rates in a closed adiabatic test cell and a theoretical attempt temperature rise rate during a pressure relief.

For a theoretical prediction of the distillation effect a theoretical number was developed. Due to this approach, model systems were generated and experimentally investigated. The experiments were carried out in closed and vented reaction calorimeters (ARSST, VSP2 by Fauske & Associates). The model systems used are tempered and gassy reaction systems, whereby concentrations of solvents and the ratio of reaction components are varied.

## 2. Theoretical Approach

### 2.1 Development of a theoretical number

In order to describe a reaction system in terms of its reaction potential and the dissipated energy by the evaporation, a theoretical number, similar to a dimensionless ratio, was developed. Eq(1) describes the simple physical relationships of the reaction system, which are necessary for the occurrence of the distillation effect. In literature there are already similar approaches. Semenov (1984) has already used a similar comparison. However, Semenov put the heat generated by a chemical reaction in relation to the heat which can be transferred through the reactor wall. Thereby, the reactor has a homogeneous temperature profile. These circumstances are described in the Semenov number. Stoessel (2008) made a statement on the relationship between the energy released during the reaction energy and the dissipated energy from the evaporation. He calculated the amount of solvent necessary to cool a runaway reaction system by means of vaporization. He also took into account the energy input by heating up the system until it reaches the design pressure. Another theoretical number that plays a significant role in phase transitions is the Jakob number (Smolsky and Sergeyev, 1962). This is a thermodynamic ratio that describes the relationship between the heat stored in the reactor and the energy dissipating through evaporation. Thereby, the resulting heat amount of a chemical reaction is not taken into account.

The new theoretical number is intended to enable a first quick check of the reaction system with regard to the risk of an increasing concentration of the reactants in the reaction system during pressure relief. It should be indicated whether there is a possibility that after a complete evaporation of the solvent during a pressure relief, there will be still enough residual energy from the chemical reaction available to heat the reaction system up. Eq (1) executes the different terms together:

$$K = \frac{|\Delta H_R|}{\sum \Delta H_{V,i} \cdot \frac{m_i}{m_{Gesamt}} + c_{p,Gesamt} \cdot \Delta T} \quad (1)$$

The equation describes the relationship between the energy input into the system by the chemical reaction ( $\Delta H_R$  in kJ/g) and the energy removed from the system by evaporation of the solvent or other evaporating components and the heat which will be needed to heat up the system from the operating temperature to the set pressure of the pressure relief device. By calculating the K value, an indication of the energy proportions of the reactor content is possible and whether there will be enough energy to heat the system up after the evaporation of the solvent. For K values greater one higher temperature rise rates might be possible.

### 3. Experimental investigation

#### 3.1 Experimental equipment

The experiments were carried out in the VSP2 (Vent sizing package 2), manufactured by Fauske & Associates. The VSP 2 consists of a stainless steel test cell, which is placed in a 4 L pressure autoclave. The test cell consisting of a thin stainless steel cup has a total volume of 110 mL. Due to the thin steel cup, a very low  $\Phi$  – factor results that makes possible the transmission of the laboratory test to the production scale without conversion factors. In order to protect the test cell from bursting, the pressure in the outer containment is quickly and accurately adjusted to the internal pressure over a dynamic pressure sensor. The test cell is heated by two heaters applied to the test cell. Here, the heating compensates the heat loss through the wall, so that the test cell can be regarded as a quasi-adiabatic system. During the tests, it is possible to supply the reaction mixture with more reactants via dosing. For the vented experiments the apparatuses had to be modified. Figure 2 shows the modifications made.

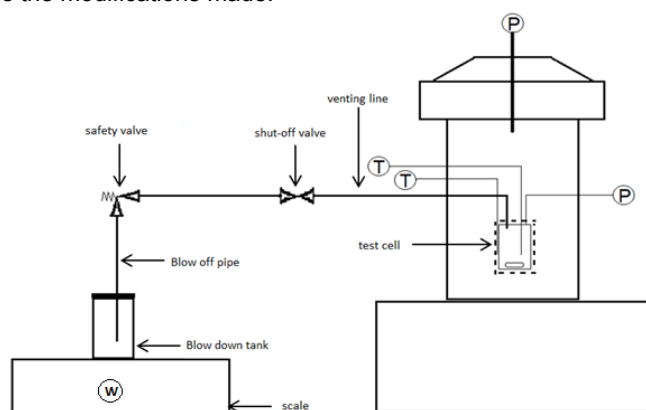


Figure 2: Modified VSP2 apparatuses for the vented experiments (consilab set up)

After the reaction mixture has been submitted as a batch, an overflow valve has been connected to a 1/8-inch pipe. The overpressure valve is designed for pressures in the range of 0.7 bar<sub>a</sub> to 17 bar<sub>a</sub>. The flowing medium is condensed via a dip tube in a suitable solvent, and a scale detects the mass profile over time. The scale signal was written with a self-programmed software to record the outflowing mass over time during the experiment.

#### 3.2 Reaction systems

To investigate the distillation effect, the exothermic esterification reaction was used. The esterification reaction of acetic anhydride with methanol is in safety engineering a very frequently used reference system for the investigation of reactive vapor pressure systems (Leung, 1989) and was selected for this reason. Some modifications of the system properties were made prior to the test. For the esterification reaction, the longer-chain alcohol hexane-1-ol was used in order to achieve an increase of the boiling point of the mixture and thus prevent the discharging of the alcohol. The reaction was carried out with a stoichiometric ratio of alcohol and acetic anhydride. In the basic course of the esterification reaction, this change had no impact. The diethyl ether which had been additionally added to the stoichiometric reaction mixture as solvent now is to discharge from the reaction mixture during the depressurization of the system. On the esterification reaction itself the diethyl ether has no influence due to its chemical structure and so it might be considered as chemically inert.

To investigate the distillation effect in the esterification model system, a large number of experiments (ARSST and VSP2 by Fauske & Associates) were performed, varying the K value from 1.5 up to 6.5. A variation of the K value was reached by varying the concentration of solvent. Three experiments will be shown as examples in the following:

For these experiments the initial concentration was equal and the K value was chosen was 6.5. The first experiment was carried out in a closed test cell of the VSP2. Therefore, the reactants were put into the test

cell, were heated up to 60 °C, and after that the runaway reaction took place. This first test represents the conservative approach to determine the maximum pressure and temperature rise rates for the design of a pressure relief device.

The second experiment took place in the modified VSP2 apparatuses (see Figure 2) with a pressure relief. Therefore, the set pressure was at 2.4 barg. This set pressure was already low, so that a reduction of the set pressure did not make sense anymore. A third experiment, where the test cell was completely open, was performed to investigate the effect of a free distillation of the solvent by the reaction energy of the thermal runaway.

As second system for the investigations of the distillation effect, the decomposition reaction of dicumyl peroxide was examined. The decomposition of dicumyl peroxide has a very high reaction energy (approx. - 220 kJ/mol) and in a system without oxygen it is a 1st order reaction, wherein the solvent has no influence on the decomposition rate (Bailey and Godin, 1955). The kinetics of decomposition of dicumyl peroxide is temperature-dependent, which in case of a cooling failure leads to a critical thermal runaway.

The decomposition can be assigned to the hybrid response systems since during the decomposition reaction gaseous methane and ethane arises. This is the decisive reason for the selection of this reaction system to study the distillation effect. Due to the high energy of decomposition, the reaction system has to be buffered by a very high boiling, inert solvent, dodecan issued. As solvent, which should evaporate already at lower temperatures ethanol was used. This should primarily discharge through the safety valve. Due to the high reaction energy of the decomposition reaction, the K value can be varied over a wide range. For the investigations in the VSP2, the K value was approximately 2.5 which may appear low but due to the intensity of the thermal runaway and the combined gas production, a higher K value could not be realized.

### 3.3 Experimental results

Esterification (Vapour pressure system)

The temperature rise rates of the respective tests were determined using a mathematical spline interpolation of the determined temperature-time curves. In Figure 3 the results of the three experiments are shown.

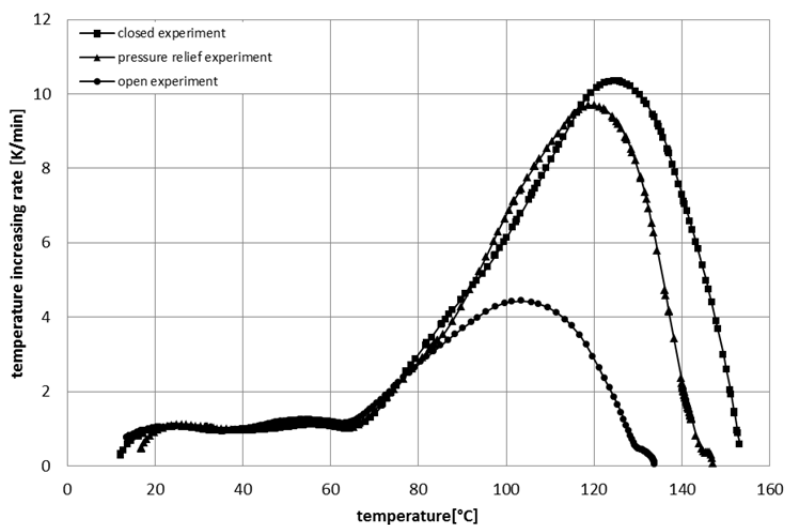


Figure 3: Results of the temperature rise rates of the different experiments of the esterification.

By comparison of the three temperature rise rates, the following statements can be made:

The distillation effect, as described in the introduction, was not observed in this reaction system. The temperature rise rates in the relieved and the open experiment were not higher than those of the closed experiment.

The following facts have a significant influence:

- The vapor pressure of the reaction mixture is not dictated by the solvent only, so the solvent cannot be easily separated from the reaction mixture.
- The reaction energy used to heat up the reaction system to the set pressure of the safety valve had already consumed about 65 % of the total energy amount of the reaction system. Consequently, the remaining amount of energy was not sufficient to remove the complete solvent from the reaction mixture and reheat with higher increasing rates.

- Products, synthesized during the runaway reaction, also discharged through the safety valve and had an additional cooling effect on the reaction mixture.

Decomposition reaction (hybrid system)

In Figure 4 the temperature rise rates of the decomposition experiments are shown. By a comparison of the temperature rise rates, it can be seen, that the temperature rise rates of the closed test were higher over the entire temperature region than those of the relieved experiments.

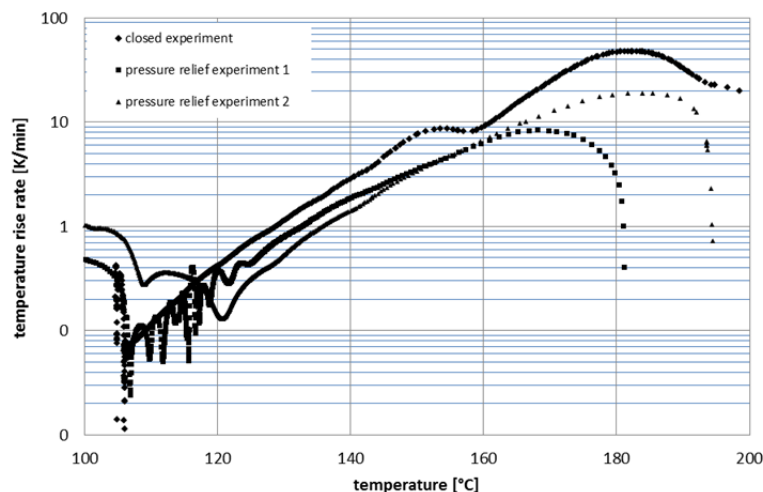


Figure 4: Results of the temperature rise rates of the different experiments of the decomposition reaction

When comparing the two relieved experiments, it can be noticed that the temperature rise rate of “pressure relief experiment 2” was higher than that of “pressure relief experiment 1”. Reason for the higher rate of temperature rise is the set pressure of the safety valve. While in the first attempt the bulk of the solvent abruptly evaporated at the end of the experiment, during the second relief attempt a uniform outflow of solvent was produced over almost the entire experimental period. Due to that fact, in “pressure relief experiment 2” to a homogeneous level swell of the reactor contents came about and a two-phase flow in the safety valve occurred. Thereby, reaction mass was also discharged from the reactor. Subsequently, no temperature rise rates higher than in the closed experiments could be reached.

#### 4. Conclusion

The theoretical number  $K$  (see section 2.1), which was developed to describe the reaction system in relation to the distillation effect, has its validity, since it first describes the basic necessary requirements for the occurrence of the effect. It indicates the ratio of the energy supply of the chemical reaction in the system and the energy dissipation by the evaporation of the solvent and other discharging components. If the ratio is greater than one, higher rates of temperature rise could in principle be achieved by a pressure relief. The main disadvantage of this indicator is the static view of the initial conditions. For this reason, the theoretical number can only be used as an indicator for the occurrence of the distillation effect. Knowledge of the chemical reaction type is also important here. It has to be either an irreversible reaction, or, a reaction the equilibrium of which lies mainly on the product side and which is not or only slightly influenced by changing pressure and temperature values. There are a variety of reaction schemes summarized in three basic types:

Type A:  $A + B \rightarrow C + D$

Type B:  $A \rightarrow B + C$

Type C:  $A + B \rightarrow C$

Types A and B were examined in this paper. The esterification reaction belongs to the type A reaction, where the resulting products can also flow as evaporated vapor through the pressure relief device and also contribute to the cooling of the reaction system. Consequently, no higher temperature rise rates were identified. The decomposition reaction of dicumyl peroxide can be assigned to the type of reaction B. Although the discharging solvent resulted in a concentration of the reaction mixture, no higher rates of temperature rise were obtained. Due to the gas production of this reaction system and the very fast thermal runaway at the

end, there is a homogeneous level swell of the reactor content resulting in a two phase flow and in a discharge of the reaction mixture.

The reaction type C is the reaction where after the evaporation of the solvent higher increasing rates are most likely. By the discharging solvent, the concentration of the reactants is increased and the resulting product, having the highest molar mass, is not able to flow through the relief device. Polymerization reactions pertain, for example, to the reaction type C. This could be a topic for further investigations.

In a reaction system solvents should be used which have a low enthalpy of vaporization and a high heat capacity. This circumstance can be explained as follows: By evaporating of solvent, little energy is taken from the system while, at the same time, the loss of solvent has a great impact on the reaction mixture's heat capacity. For instance the heat capacity may adopt smaller values. In a progressive thermal runaway reaction thereby a more rapid temperature rise results.

Furthermore, the solvent used must represent the component with the highest vapor pressure in the system, otherwise educts or products can be discharged through the pressure relief, which also contributes to a cooling and, on the other hand, could reduce the reaction rate.

Another important condition to be met by the system for the occurrence of the distillation effect is that the solvent has to be easily removable from the reaction phase. In the esterification reaction, it was observed that the system vapor pressure did not behave as expected since it was difficult to separate the diethyl ether, the solvent in this reaction system, from the reaction mixture.

A high opening pressure of the relief device makes the system uncritical with respect to the distillation effect because a portion of the reaction energy is consumed by heating the entire reaction mixture. The experimental tests could confirm that early relieved reaction systems have a higher temperature rise rate than relieved systems with higher set pressures. With this observation, it can be concluded that hybrid systems with gas production, display more tendency towards the distillation effect. By gas formation and the resulting rapid pressure increase inside the reactor, the set pressure of a relief device is reached more quickly.

In conclusion, the statement can be made, that for the occurrence of the distillation effect a variety of factors have to come together. The error for the calculated discharging area that results if a wrong temperature rise rate is selected at the maximum allowable pressure is in most cases negligible. It can be stated that the distillation effect can be expected only in a few reaction systems. The current approach to the design of pressure relief devices on the basis of closed adiabatic test cells is sufficient.

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