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Online Model-Based Process Safety Concepts in Polymerization

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Summary: To safeguard runaway reactions in industrial scale, qualified methods have to be used. While mechanical safety devices are usually installed, their design may be problematic as the runaway kinetics must be known. This may not be the case for many processes due to the required flexibility and possible unanticipated deviations from recipes. It is shown that runaway kinetics can be very fast and can lead to high conversions. Therefore, a method is proposed that does not depend on kinetics but limits the amounts of unreacted monomer in the reactor by monitoring the conversion and by quantitatively determining the hazardous potential. If a potential violation is observed, feeds to the reactor are interrupted.

Keywords: calorimetry; emulsion polymerization; kinetics (polym.); reactor safety; thermal runaway reaction

Introduction

Polymerization reactions are exothermic in nature. Whenever cooling fails, a self-sustaining uncontrolled runaway reaction may occur, leading to increased temperatures. With these temperatures come increased vapor pressures. Furthermore, at elevated temperatures secondary reactions may occur, which further generate heat and/or non-condensable gases. This will lead to the generation of pressure in sealed or inadequately vented reactors, possibly leading to a hazardous loss of containment of the reactor contents in case the design parameters of the reactor (temperature or pressure) are exceeded. While fortunately not common, runaway polymerizations make up a large part of industrial incidents.[1]

Therefore, it is of paramount importance to safeguard industrial polymerization reactors. The determination and evaluation of all the potential hazards involved in operation of a plant is an important step in the design of the polymerization process and is part of the safety lifecycle.[2] The process risks should be mitigated to a residual risk level that is below the tolerable risk level.

There are several methods available to safeguard a reactor. A very common method to safeguard the reactor is to use pressure relief valves or rupture discs on top of the reactor. However, this is not necessarily a good option for all polymerization reactors. The design of the pressure relief valve or rupture disc depends on the expected kinetics during a runaway reaction. The question is, what to expect?

For batch polymerization reactors which are used for a single product with a single monomer, information on the runaway behavior may be gathered relatively easily. However, in case the reactor is used for many different recipes involving many different monomers, as is for instance typical for an emulsion polymerization reactor to fulfill the wide range of application property requirements from customers, it may prove difficult to determine the worst-case scenario. This is especially problematic since deviations from the normal course of reaction can lead to situations that are by far worse than expected based on the recipe but have to

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be taken into account nonetheless. These deviations may include less inert material, more monomer or a change in monomer composition that is more hazardous. While Distributed Control Systems (DCSs) or Programmable Logic Controllers (PLCs) usually show good behavior, they do not conform to the Safety Integrity Levels (SIL) required by the process to reduce the risks to an acceptable level[3] and cannot guarantee sufficiently that the process is run according to recipe. Furthermore, mechanical safety devices will relieve the reactor, but the reactor contents must be released to a safe place. Otherwise, the reactor contents could form an explosive cloud that could be ignited, due to the monomers involved in the polymerization. Dispersion calculations must be evaluated.

Here, we would like to give more information on what runaway kinetics to expect as well as to what conversion level a runaway reaction may reach. Based on these considerations we would like to present an alternative method for mitigating risks involved with a runaway polymerization reaction, based on examples from emulsion polymerization. However, the method may be applied to any polymerization process.

Considerations on Runaway Kinetics for Emulsion Polymerization

The rate of polymerization for an emulsion polymerization is determined by the propagation rate coefficient, the monomer concentration in the particles, the average number of radicals per particle and the number of particles in the reactor. In a recent paper,[4] the hazardous potential of an emulsion polymerization has been determined with a back-of-an-envelope calculation and as a first estimate the rate of polymerization equals $0.72\ \mathrm{mol \cdot L^{-1} \cdot s^{-1}}$. For a better understanding of this value, this number can be transformed into an adiabatic temperature increase rate of $17\ \mathrm{K \cdot s^{-1}}$ or also $1.0 \times 10^3\ \mathrm{K \cdot min^{-1}}$. This is an extraordinarily high temperature increase rate that at first glance looks much too high. The reaction would be over in a matter of seconds.

Therefore, this number should be compared with an example from an actual runaway reaction at industrial scale.[4] Here, a seeded butyl acrylate recipe with aimed particle size of approximately 3×10^2 nm and aimed 50% final solids content was polymerized at 70 °C with sodium persulfate as initiator. Although initiator was being fed, the reaction did not start correctly which finally led to a runaway reaction as depicted in Figure 1. Although the jacket was switched to full cooling, the temperature increased very fast indeed and a maximum temperature increase rate of approximately $65\ \mathrm{K \cdot min^{-1}}$ was observed. A final temperature of 135 °C was reached. In this case, the contents were contained within the reactor.

It should be mentioned that the reaction described here by no means constitutes the worst case that can be envisaged for emulsion polymerization but just a random runaway reaction that has been observed. For instance, the starting temperature for the excursion could be higher or the aimed particle size could be smaller. Therefore, the worst case estimate of $1.0 \times 10^3\ \mathrm{K \cdot min^{-1}}$ that was obtained above seems to be off only by about or even less than a factor of ten! This must lead to the installation of very large safety relief valves or rupture discs when these constitute the sole safeguarding measure of a reactor, especially for larger reactors.

Conversion during Runaway Emulsion Polymerization

An important question for runaway reactions is to what extent this reaction continues, since this defines the final adiabatic temperature and pressure that may be reached. This is especially interesting for emulsion polymerization reactions, in which persulfate is often used as initiator. At higher temperatures around 130 °C and above, the

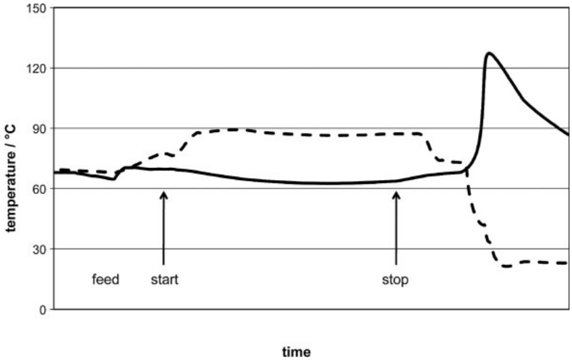

Figure 1.
The reactor temperature (full line) and jacket outlet temperature (dotted line) before and during a runaway emulsion polymerization reaction. The arrows indicate the times at which the feed is started and stopped.

decomposition of the initiator is very rapid[5] and no further initiation of the reaction by the initiator is expected due to its depletion. At these temperatures, thermal initiation of monomers[6] may be too slow to promote the reaction enough, preventing the runaway reaction of reaching full conversion.

If proof can be obtained that an inherent boundary for the maximum conversion during a runaway emulsion polymerization exists, this would be of great interest to industry, as on this basis new reactors could be installed with lower design parameters for temperature and pressure, leading to lower capital investment. In order to prove or disprove the existence of this boundary, several experiments on laboratory scale (3 L) have been performed. Earlier Vent Sizing Package (VSP) experiments at smaller scale did not provide enough resolution to be able to track conversion sufficiently at higher temperatures.

The 3 L lab scale reactor is placed in an isolated box which can be heated electrically. The heat carrier oil is heated by a high performance once-through thermostat with 9 kW heating power (Huber unistat T305HT). All temperature measurements are measured with high accuracy. The reactor is equipped with the laboratory DCS Lab Manager from Hitec Zang, which allows for easy implementation of temperature control strategies for near adiabatic conditions.

The key for performing meaningful experiments is to be able to operate the laboratory reactor adiabatically. Performing adiabatic experiments in lab scale is difficult compared to production scale. Lab size reactors have much higher ratios of heat exchange area to reactor volume and of reactor content to reactor steel mass, leading to much higher heat losses. The heat losses of the reactor contents can be divided in two parts: a) heat loss to the environment due to convection and radiation and b) heat loss due to heating up the reactor steel mass.

Heat is transferred to the environment. To compensate for the steady-state heat loss to the environment with T_{amb}, the temperature of the heat-carrier oil T_{oil} entering the reactor has to be slightly higher than the temperature T_R inside the reactor. This is indicated in Figure 2.

In addition to the heat transfer to the environment, heat from inside the reactor is used to heat up the reactor walls. Due to the disadvantageous mass ratio this cannot be neglected but must be compensated. Even in the case that the heat-carrier oil has always the same temperature as the reactor charge, heat will be transferred from both sides of the reactor wall to heat up the wall during a runaway. Thus, during a runaway the temperature of the heat-carrier oil must always be some degree higher than the temperature inside the reactor. This is

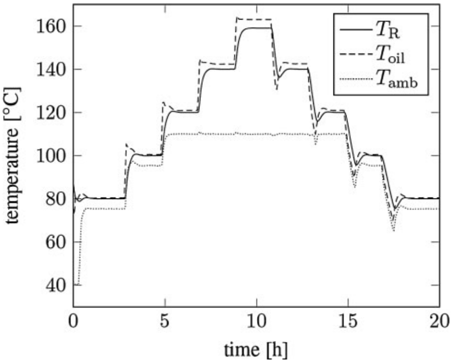

Figure 2.
Closed loop control of the reactor temperature to determine the necessary temperature of the heat-carrier oil for adiabatic conditions inside the reactor.

indicated in Figure 3 using results from simulations.

All experiments were based on a recipe with varying ratios of styrene to butyl acrylate as well as monomer to water (to achieve different theoretical maximum temperatures) with 80 °C as starting temperature. While pure styrene recipes reacted slowly, recipes with pure butyl acrylate were very fast. Again temperature increase rates of up to $100\,K \cdot min^{-1}$ have been observed.

From the experiments, it became clear that while initiator is depleted, the reaction is very fast as well and can lead to high temperatures, well over 170 °C. An example of a runaway reaction is given in Figure 4. Based on these experiments, reaching a conversion of around 100% during a runaway reaction cannot be excluded a priori.

Online Model-Based Process Safety Concept

Due to the fast kinetics and high conversions that can potentially be reached during a runaway reaction, safeguarding a large reactor with a safety relief valve or rupture disc proves difficult due to the sizes required. An alternative method has been developed to avoid having to use such large mechanical safety devices by limiting the amount of unreacted monomer present in the reactor. The hazardous potential of a polymerization is determined by this amount. While large amounts of monomer would lead to uncontrolled runaway reactions, smaller amounts would also lead to an increase in temperature and pressure, but only to a limited degree. This smaller increase can usually be handled by the reactor, as the resulting temperature and pressure would still be below its design parameters.

Within the alternative safety concept, the first step is therefore the determination of the residual amount of monomers. Several methods are available for the monitoring of a polymerization reaction.[7] While direct measurement with spectroscopic methods of the individual concentrations of monomer can be very helpful, these mostly depend on complicated mathematics

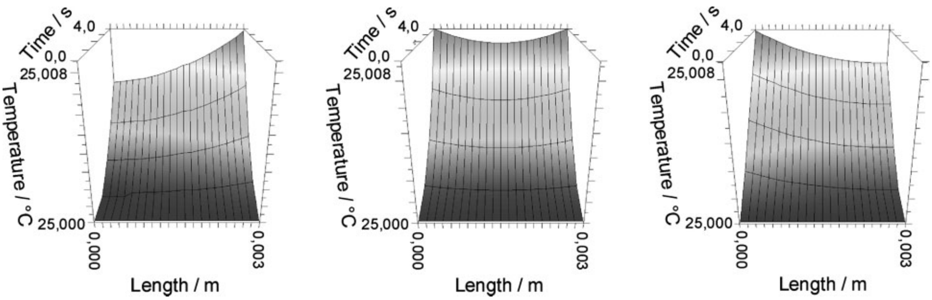

Figure 3.
Schematic representation of the temperature profile in the reactor wall as function in time for a) constant oil temperature, b) oil temperature equal to temperature in reactor, c) oil temperature higher than reactor temperature. The reactor contents are on the right side, the oil on the left side of the wall.

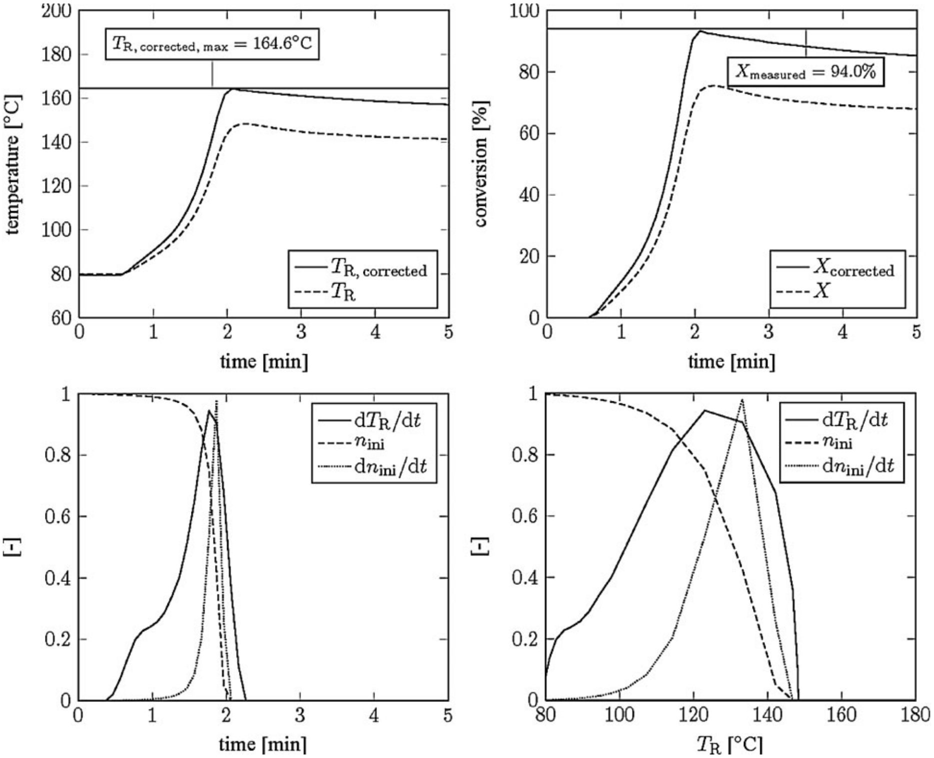

Figure 4.

Runaway reaction of a butyl acrylate dispersion with the reactor temperature T_R and the conversion X. A correction is required to compensate for the imperfections of the laboratory calorimeter. The conversion is compared with data from sampling the solids content. Furthermore, the temperature increase rate is compared with the amount of initiator n_{ini} and its change rate.

and equipment that do not fulfill the requirements under IEC 61511-1[3] regarding usage within a Safety Instrumented System (SIS) with an appropriate SIL level. A straightforward but indirect method is to measure the conversion with the heat balance method (see Figure 5). This method only requires the measurements of the mass flows to the reactor and their temperatures, the temperature of the reactor contents as well as the cooling/heating medium flow rate and its inlet and outlet temperatures. More importantly, the implementation in a fail-safe PLC (FPLC) with its limited programming language is not overly difficult. This is currently the method of choice.

As the heat and mass balances obtained this way allow the determination of the actual state of the reactor contents, it now is possible to determine what could poten-

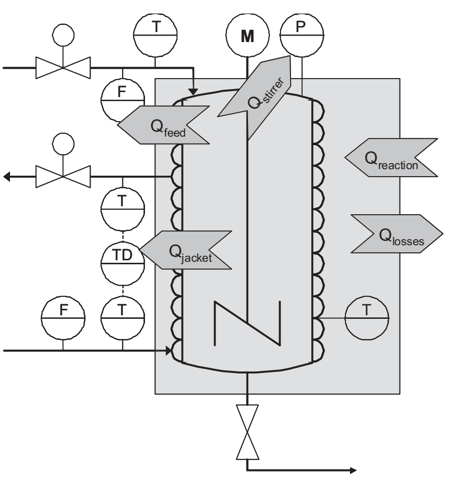

Figure 5.

Schematic overview of the heat balance method and its important heat flows.

tially happen during a runaway reaction at any moment during the course of a reaction. For this second step, the amount of reaction enthalpy that is still available for release during a potential runaway reaction is determined. Based on this reaction enthalpy, the expected adiabatic runaway temperature and pressure can be calculated and can be compared with the design limits of the reactor. If either the calculated adiabatic temperature or pressure is higher than these limits, the corresponding amount of residual monomer is too high. As soon as this situation occurs, all energy containing feeds to the reactor must be closed to prevent a possibly hazardous situation.

The final adiabatic runaway temperature $T_{adiabatic}$ can be calculated straightforward as

$$T_{adiabatic} = \frac{(1-X)\cdot \Delta H_r}{m \cdot c_{p,mix}} + T_R \qquad (1)$$

with X the determined conversion, ΔH_r the total reaction enthalpy from the monomers fed to the reactor, m the mass of the reactor contents and $c_{p,mix}$ its specific heat capacity. However, the calculation may become more complicated if other factors are taken into consideration as the heat of vaporization or the temperature dependence of the specific heat capacity, which both yield lower temperatures.

For the pressure, such easy calculations are possible as well. However, in this case the same amounts of monomer, polymer and other ingredients are assumed to be present as at the start of the runaway reaction at reactor temperature. A calculation on this basis but now at the final adiabatic runaway temperature yields a very large overestimation of the adiabatic pressure. The overestimation of the hazardous potential leads to an early shutdown of the batch or requires a high pressure design of the reactor. There would be no advantage from the model-based safety concept.

Therefore, models have been developed to describe the pressure behavior during runaway. At the maximum adiabatic temperature, for an emulsion polymerization all monomer is converted and the pressure is determined by the water vapor pressure and the contribution of the non-condensable gases. Before reaching full conversion, temperatures are still high and monomer is still present, so the maximum pressure is reached somewhere between the actual reactor temperature and the maximum adiabatic temperature.

Pressure Modeling

For emulsion polymerization, four contributions are determining the pressure: a) the vapor pressure of the continuous aqueous phase, b) the compression contribution of nitrogen or other non-condensable gases, c) the vapor pressure of the monomers which are dissolved in the organic latex particles and d) the vapor pressure of a separate monomer phase, if present. The contributions from water and nitrogen are straightforward to be calculated, based on the reactor temperature and the filling level in the reactor. Due to their consumption, the contribution from the monomers is requiring a stepwise approach along the conversion of monomer during the runaway reaction with calculation of the pressure at each step and keeping the maximum pressure. This is indicated schematically in Figure 6.

In principle, there are no limitations to the pressure calculation method and its level of detail. Nevertheless, the contribution of the different phases to the overall pressure decides on the advantages of a model based safety system. Figure 7 shows

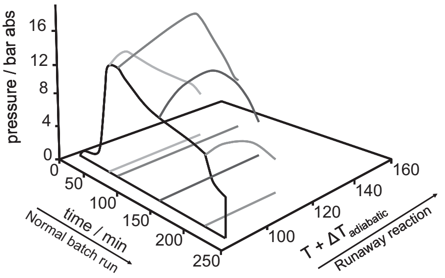

Figure 6.
Schematic description of temperature and pressure evolution during a runaway reaction.

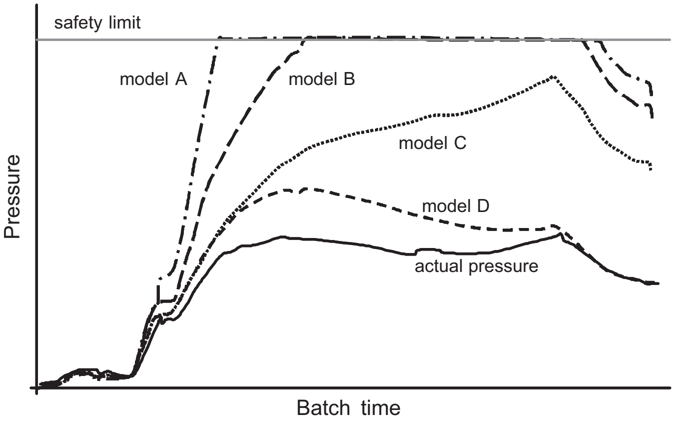

Figure 7.
Influence of different pressure models on the calculated adiabatic runaway pressure during a batch and comparison with actual pressure and the safety limit.

the effect of different assumptions on the calculated adiabatic pressure rise compared to the safety limit.

As already mentioned above, a conservative model (model A), assuming a final temperature and assuming that the composition of the liquid phase at this final temperature is equal to the overall composition in the reactor leads to a rather high adiabatic pressure rise. A calculation, in which the remaining conversion is divided into several steps (model B) yields lower runaway pressures, but may still lead to too high pressures to allow operation. More realistically but still conservative is to additionally invoke flash calculations (model C) which reduces the pressure by adaptation of the composition of the liquid monomer phase towards less volatile monomers. On the other hand, conversion only takes place in the monomer containing particle phase, which leads to an increase in pressure at later stages as the monomer mixture in the reactor becomes enriched in volatile monomers as these are overrepresented in the gas phase.

Another gain is to consider the interaction of monomer and polymer in the particle phase as this usually leads to a pressure depression. This can be based on Flory–Huggins solution theory[8] (model D) or on more modern theories.[9]

The only limits to the pressure model are the effort to generate the model and even more importantly the calculation power of the FPLC used in the installation. While current FPLCs could actually perform many of the calculations required for advanced pressure models, their engineering tools usually do not allow these calculations due to the limited programming language available. While it is possible to write the software in other languages, this would no longer fall under the international standard IEC 61511-1.[3] Software development for safety applications falls under the IEC 61508-3 standard,[10] which requires an extreme effort that may not be worthwhile to pursue for individual applications.

Based on the online models in the SIS, a good estimation is available for the actual hazardous potential of a batch at all times during this batch. This allows the process to be run closer to the design limits of the reactor while still being safe.

Conclusion

The alternative online model-based process safety concept does not require any kinetic information on the runaway reaction but looks at the maximum attained values for both temperature and pressure. No rigorous investigation in the runaway kinetics is required and the method can be applied for a whole range of recipes. This flexibility is a major advantage. Furthermore, as the hazardous potential is known quantitatively, the processes can be run closer to the design parameters of the reactor.

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