Simulation of Decomposition Reactions considering the Residual Cooling Capacity of Industrial Reactors

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In chemical production plants, process safety is one of the most important goals. A classical concept within the field of thermal process safety is the scenario of a cooling failure by Gygax, see Figure 1 [1]. Amongst the reaction temperature T_R, the maximum temperature of the synthesis reaction (MTSR) and the adiabatic decomposition temperature (ADT24) are important characteristics in this concept. Knowing the ADT24, the maximum allowable temperature for the process T_{Exo} can be derived. The technical rule for plant safety (German: Technische Regel für Anlagensicherheit (TRAS) 410) suggests to limit the T_{Exo} 10 K below the ADT24 [2].

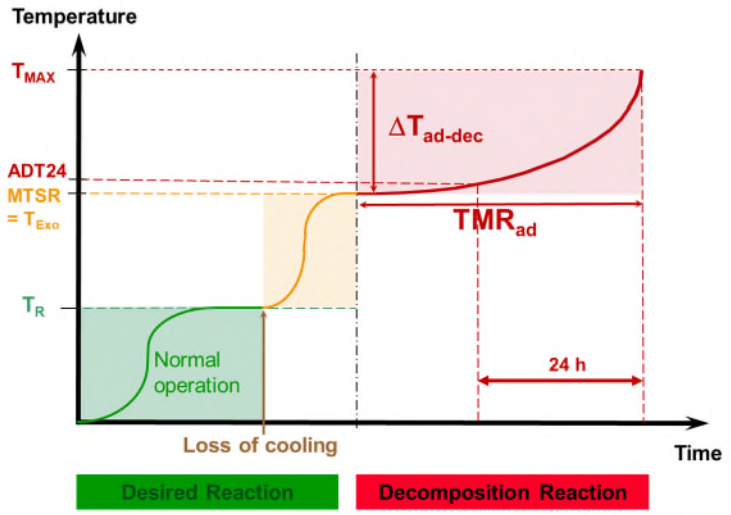

Figure 1: Scenario of a cooling failure by Gygax [1]

The TRAS 410 also emphasizes to consider the heat loss of the system when determining the maximum allowable temperature T_{Exo}. For this reason, a study has been performed, investigating the impact of the residual cooling capacity of industrial reactors on the T_{Exo}. Residual cooling capacity describes the passive cooling capability of the system after failure of active cooling facilities, particularly due to the heat loss to the environment, i. e. ambient cooling.

In this study, alkoxylation reactions were investigated with respect to the scenario of a cooling failure. In alkoxylation processes, a nucleophilic compound like an alcohol or amine is converted with an alkylene oxide like ethylene oxide or propylene oxide, for example. The reaction can be catalyzed by Bronsted bases such as sodium hydroxide or potassium hydroxide. Due to the high reaction enthalpy, e. g. 92 kJ/mol ethylene oxide, these processes are often conducted in a semi-batch mode with dosing control. At BASF, alkoxylation processes are safeguarded with a model-based concept [3]. The model determines the free oxide concentration in the reactor in every moment of the reaction. The oxide dosage is regulated such that in case of a cooling failure the runaway of the synthesis reaction would lead to the maximum allowed temperature T_{Exo}. At this temperature, the decomposition of the reaction mixture starts slowly with a rather small heat release rate.

In alkoxylation processes, we use a slightly different definition of the ADT24, which is more conservative than the definition given in TRAS 410. According to TRAS 410, the ADT24 is the temperature at which the time to maximum rate (TMR) at adiabatic conditions equals 24 hours [2]. Following this approach, the T24_T_{Design} is defined as temperature, at which it takes at least 24 hours to reach the reactor design temperature. The maximum rate of the decomposition reaction is observed at temperatures larger than 250 °C, usually. Because of this conservative definition and after having conducted sophisticated thermal analyses of the decomposition reaction for each polyether polyol, the T24_T_{Design} is implemented as maximum allowed temperature T_{Exo}.

The decomposition reaction was investigated in an alkaline environment with calorimetric techniques. For different kinds of polyether polyols, a formal kinetic model was generated describing the decomposition reaction. It has to be emphasized that in alkaline environments the decomposition may become relevant at lower temperatures than in neutral ones. On the other hand, the specific heat loss due to ambient cooling was determined experimentally for various industrial reactors. This data was used to perform numerical simulations for the prediction of the decomposition reaction for various product-reactor-combinations. For modelling and simulation, the software code from Cheminform St. Petersburg “Thermal Safety Series-Advanced Reaction Kinetics Simulation (TSS-ARKS)” was used. The simulations were applied to derive the maximum allowed temperature T_{Exo}. Depending on the product-reactor-combination, in the case with residual cooling the T_{Exo} may be 10 K to 20 K higher than the T_{Exo} in the ideal adiabatic case, see Figure 2. When additional countermeasures, like independent emergency cooling or drainage/quench systems, are provided, the T_{Exo} may be increased by approximately 50 K compared to the ideal adiabatic case.

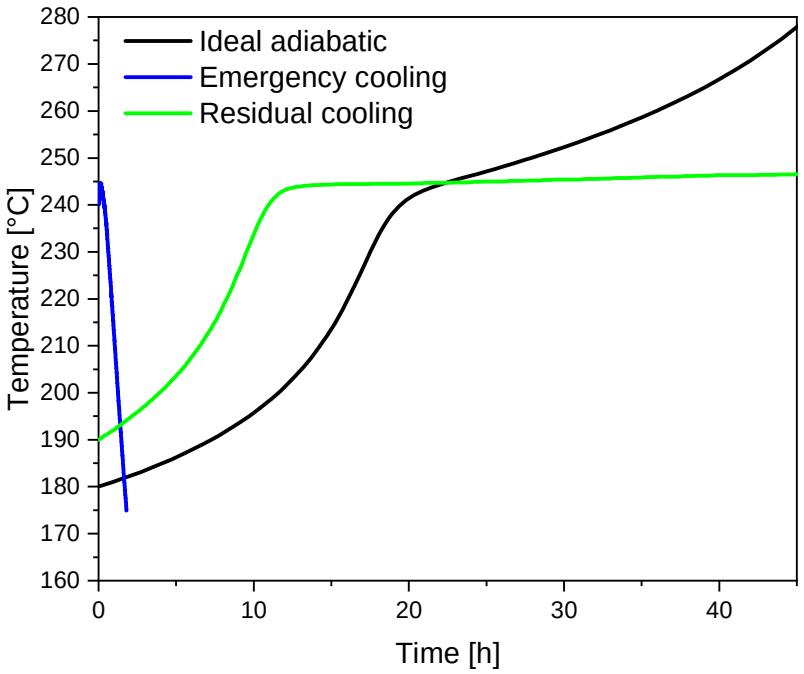

Figure 2: Simulation of the temperature-time curves of the decomposition reaction of a polyether polyol for 3 cases: ideal adiabatic, emergency cooling, residual cooling (35 m³ reactor with insulation). The initial temperature of each curve corresponds to the maximum allowed temperature T_{Exo}.

References

1. Gygax, R., *Chemical reaction engineering for safety.* Chemical Engineering Science, 1988. **43**(8): p. 1759-1771.
2. Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, *Technische Regel für Anlagensicherheit (TRAS) 410.* Komission für Anlagensicherheit, Bundesanzeiger, 2021.
3. Lötgering-Lin, Salg et al. *Modellbasierte Absicherungskonzepte für Semi-Batch-Alkoxylierungen*. in *14. Fachtagung Anlagen-, Arbeits- und Umweltsicherheit*. 2019. Köthen: Dechema.