

Knowing and Controlling the Risks of Semi-Batch Alkoxylation Reactions

Oliver Lötgering-Lin*, Steffen Salg, Christian König, Hannes Buchholz, Markus Gödde, Oliver Odenwald, Wilfried Sager, Andreas Brodhagen, Thomas Heitz, Roland Ries

BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany
 oliver.loetgering-lin@basf.com

In this work, major risks specific to alkoxylation reactions are summarized. Special focus is given to the risk of a thermal runaway of the synthesis reaction and the potentially following exothermal decomposition of raw materials, intermediates and products. The concept presented is basis for safeguarding alkoxylation reactions globally within BASF (certified by DEKRA Industrial). As an integral part of BASF's safety concept, the importance of quantifying the thermal decomposition risk is highlighted and a model-based approach to control that risk by limiting the oxide accumulation is presented.

1. Introduction

Although the alkoxylation process has been well established for several decades in the chemical industry, severe plant incidents still occur. The most recent accident happened on January 14th 2020 at an IQOXE plant in Tarragona, Spain. An explosion occurred in an ethoxylation reactor and ignited a nearby propylene oxide storage tank causing three fatalities (Ebel, et al., 2020) (Neyraval, et al., 2022).

Herein, we summarize hazards of the alkoxylation process and present a model which was developed within BASF over the last two decades to safeguard alkoxylation reactions (Salg & Lötgering-Lin, 2022). The developed thermodynamic model calculates the amount of unreacted, accumulated alkylene oxide within the reactor based on current process conditions. Unreacted alkylene oxide poses a major risk, as, in case of e.g. insufficient cooling, an uncontrolled reaction of accumulated alkylene oxide leads to a dramatic rise in temperature (thermal runaway). Calorimetric measurements are used to define safe post-runaway temperatures taking into account the serious effects of a thermal decomposition after the runaway. Based on the calculated alkylene oxide accumulation, a runaway model is applied to make sure that the process is kept within the defined safe post-runaway limits. The authors highlight that detailed risk assessments are crucial for every product/reactor-combination, taking into account the respective batch size. The given overview of risks that are related to alkoxylation processes does not claim completeness. Alkoxylation is the chemical reaction of an alkylene oxide with a nucleophilic component. In most cases alcohols (X=O) or amines (X=NH) are used as nucleophilic components. Ethylene oxide (R'=H) or propylene oxide (R'=CH₃) is typically used as a reagent (ethoxylation or propoxylation respectively). The use of butylene oxide (R'=CH₂CH₃, butoxylation) or higher epoxides is less common. Main applications are surfactants, polyether polyols for polyurethane applications and lubricants (Ionescu, 2016).

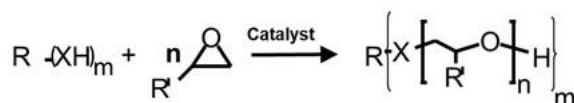


Figure 1: General reaction of an alkylene oxide with a nucleophilic component

Alkoxylation reactions are carried out both as a semi-batch with a typical batch size of 5 – 200 m³ or as continuous process. In most cases basic catalysts such as sodium hydroxide, potassium hydroxide or caesium hydroxide are used. Alternatively, multimetalcyanid-catalysts, e.g., double metal cyanide catalyst (DMC) or Broensted- or Lewis-acid catalysis are also utilized. The most relevant hazards for alkoxylation reactions are uncontrolled decomposition reactions (gas or liquid phase) as well as uncontrolled polymerization (i.e., thermal runaway) reactions (Salzano, et al., 2007) (Maestri & Rota, 2017).

Ethylene oxide (EO) can explode even in the absence of oxygen if an ignition source of sufficient energy is present. This self-decomposition is associated with a rapid increase in temperature and pressure and formation of decomposition gases such as carbon monoxide, methane and hydrogen as well as ethane, ethene and soot in smaller amount. The minimum ignition energy for the self-decomposition of EO vapors is influenced by pressure and temperature. Pressure increase factors of 7 or higher are possible according to studies by Pekalski et al. and can lead to severe explosions (Pekalski, et al., 2005). Therefore, avoidance of gas phase decomposition has to be a substantial part of the safety concept. This is of equally high importance for EO transfer in pipelines. If liquid EO is heated locally, the resulting vapor bubbles which are under high pressure can be ignited via external heat input. This can cause flame propagation into other plant components (BG Chemie, 2007). Protective measures have to be taken to prevent or limit the effect of decomposition reactions or uncontrolled polymerizations. Therefore, reaction temperatures, pressures and alkylene oxide concentrations have to be monitored and limited by process related measures, process control systems and constructive arrangements. The adequate protective measures have to be evaluated in a risk assessment based on the specific hazard potential (BG RCI, 2022).

2. Modelling normal operation

The key quantity in modelling alkoxylation reactions is the amount of free oxide inside the reactor. The amount of free oxide is related to the reaction rate and is thus of relevance with respect to process optimization. At the same time, it is the crucial quantity and to be limited in terms of process safety. Direct measurement of the amount of unreacted oxide within a process is difficult, especially in sufficient quality and reliability if applied as a safety measure (redundancy). Thermodynamic models can fill this gap to determine the amount of unreacted oxide from reliably obtainable process observables like dosed masses (e.g., starter material, oxide etc.) temperature and pressure. A typical semi-batch alkoxylation reaction consists of the following process steps: Empty reactor & leakage check (1), Filling of the reactor (2), Preparation of starter by evaporation of solvent (high temperature, low pressure) (3), Inertization (4), Heating up to initial reaction temperature (5), Oxide addition and reaction (6), Postcooking & Postprocessing (e.g., oxide stripping) (7), Cooling, Emptying & Cleaning (8). Accurate knowledge of the reactor content is crucial for a thermodynamic model. Hence, before adding any material to the reactor, the reactor needs to be completely clean and empty (except for nitrogen) and all materials dosed in the following step need to be monitored & measured. In most cases, water dosed along with the catalyst is stripped in a dewatering step. If no dewatering takes place, the mass of water prior to oxide dosing must be considered. This includes water the catalyst is dissolved in, water from the formation of alcoholate and separately dosed water.

In the inertization step the reactor is pressured up to a certain pressure p^0 at a specific temperature T^0 . This inertization with nitrogen can be thermodynamically described by, e.g., the modified Raoult's Law, as

$$y_i p^0 \phi_i = x_i \gamma_i p_i^{sat}(T^0) \quad (1)$$

for a component i with y_i as molar concentration in the gas phase, p^0 as total pressure in the inertization, ϕ_i as fugacity coefficient, x_i as molar concentration in the liquid phase, γ_i as activity coefficient and p_i^{sat} as saturation pressure at the given inertization temperature T^0 . Given the typically high temperatures and rather low pressures, it is reasonable to assume an ideal gas phase, described by the ideal gas law. The liquid phase cannot be considered ideal and activity coefficients needs to be determined (VLE-measurements). Here i can be the starter (e.g., alcohol), co-starter material (e.g., water) or a volatile, non-reactive component. For nitrogen, a concentration independent activity coefficient according to Henry's law (H_{N_2}) can be applied due to the low concentrations of nitrogen in the liquid phase. The activity coefficients, derived from VLE experiments (catalyst-free) or thermodynamic models (e.g., PCP-SAFT), are highly substance dependent. At infinite dilution they range from 10^{-7} 1/Pa to 10^{-11} 1/Pa for N₂ and 0.01 to 10 for alkylene oxide

$$p_{N_2} = x_{N_2} / H_{N_2} \quad (2)$$

If the masses of all dosed liquid starter materials are known, the total amount of nitrogen (in the gas phase as well as dissolved in the liquid phase) after the inertization step, $n_{N_2}^0$, can be determined from the inertization

process pressure p^0 and inertization process temperature T^0 by combining Dalton's law, Eq(3), with Eq(1) and Eq(2) using a simple flash algorithm.

$$p(T) = p_{N_2}(T) + p_{Pol}(T) + \sum p_{vol}(T) \quad (3)$$

Depending on the specific recipe, the inertization process pressure p^0 consists of the partial pressure of nitrogen p_{N_2} , the starter material or polyol p_{Pol} and further volatiles p_{vol} such as water.

This initial amount of nitrogen is crucial for a sound model-based safety concept as it provides the baseline (in terms of pressure) for all subsequent calculations. Therefore, it is necessary to know all constituents in the reactor during this inertization step including their respective vapor pressures, p_i^{sat} contributing to the pressure during the inertization. To guarantee a minimal oxide reaction rate the reaction mixture is heated up to a minimal temperature. That minimal temperature has to be chosen sufficiently high such that the vapor pressure of the oxide is a representative indicator for its accumulation. Besides the nitrogen from the inertization step, $n_{N_2}^0$, also nitrogen dissolved in the alkylene oxide that is dosed to the reactor, $n_{N_2,A}$, needs to be considered. To this end, a simple VLE calculation of the N₂/oxide-system in the tank farm given the storage pressure and storage temperature (either safeguarded min/max values or online data) needs to be done. Knowing the total amount of nitrogen in the reactor, $n_{N_2} = n_{N_2}^0 + n_{N_2,A}$, the same set of equations (Eq(1) and Eq(2)) can be applied to model the oxide dosing. In contrast to the inertization step, during oxide dosage the amount of free oxide $n_{A,Acc} = n_{A,gas} + n_{A,liq}$ is the result of the flash calculation at pressure p , temperature T and batch progress $n_{A,dosed}$. Obviously, with increasing filling level during the batch, the reduction of the gas phase volume needs to be modeled precisely. The change of thermophysical properties (most importantly gas solubilities and densities) with temperature T and changing degree of alkoxylation θ must be considered; derived either from experiments or thermodynamic models (e.g., SAFT-based equations of state (Gross & Sadowski, 2001)). The accuracy of the applied thermodynamic models must be evaluated against measurements of relevant thermophysical properties for starter, intermediates and product ($0 < \theta < \theta^{product}$). Within a sensitivity analysis (also to be implemented in a safety instrumented system, SIS) safety margins are calculated from the derived property data uncertainties affecting the calculated maximum temperature and pressure increase when evaluating a runaway reaction of the accumulated oxide (more details in chapter 4).

3. Quantification of hazards

The reaction enthalpy of the alkoxylation reaction is about -95 kJ/mol ethylene oxide (l) or -121 kJ/mol ethylene oxide (g). The decomposition of ethylene oxide leads to the formation of small, mainly gaseous compounds: $C_2H_4O(l) \rightarrow \frac{1}{2} CH_4 + CO + H_2 + \frac{1}{2} C$, $\Delta H_R \approx -132 \frac{kJ}{mol}$

As the decomposition of the reaction mixture leads to the same products as the decomposition of ethylene oxide, the expected reaction enthalpy for the decomposition of the reaction mixture can be calculated by using Hess's law. Based on this, a reaction enthalpy of -37 kJ/mol is to be expected from the thermal decomposition of intermediates. Uncontrolled reactions of starters, intermediates or final products may lead to a considerable energy release and pressure buildup.

The hazards arising from a runaway of the synthesis reaction or a thermal decomposition of reactants, reaction mixture or final product can be quantified using calorimetric techniques. These hazards are usually discussed in the context of the scenario "loss of cooling" which can be described with the classical concept of a cooling failure as developed by Gygax (Gygax, 1988). For the BASF alkoxylation safety concept, the scenario is modified slightly with regards to the ADT24. According to the technical rule for plant safety (TRAS 410, 2012), the ADT24 is the temperature at which the time to maximum rate (TMR) at adiabatic conditions equals 24 hours (Gygax, 1988). Following this approach, the $T_{24_T_{Design}}$ (in the following referred to as T24) is defined as a maximum temperature, at which it takes at least 24 hours to reach the reactor design temperature. The modified scenario of a cooling failure is visualized in Figure 1 (left).

It has to be ensured to derive the T24 with a sample representing the worst case. This means, the thermally most instable composition has to be investigated, which may be present directly at the beginning of a batch, during the course of the reaction or at the end, represented by the starter material, an intermediate polyol or the product respectively. After having conducted sophisticated thermal analyses of the decomposition reaction for each polyether polyol, the T24 is implemented as maximum allowed temperature after the runaway (see chapter 4). The maximum pressure increase during the runaway p_{max} of synthesis reaction has to be limited so that the relief pressure of the safety valve p_{PSV} is not reached. Consequently, the release of toxic and flammable material is prevented.

$$T_{max} < T_{24_T_{Design}} \leq T_{Design} \wedge p_{max} < p_{PSV} \leq p_{Design} \quad (4)$$

However, an accelerating decomposition reaction may trigger the safety valve. Pressure release is not sufficient to control the decomposition reaction, which leads to a drastic pressure increase. After the runaway of the synthesis reaction, additional measures must be taken to prevent the decomposition reaction. These measures must be defined in individual safety concepts before start-up of a process depending on the equipment and chemicals used.

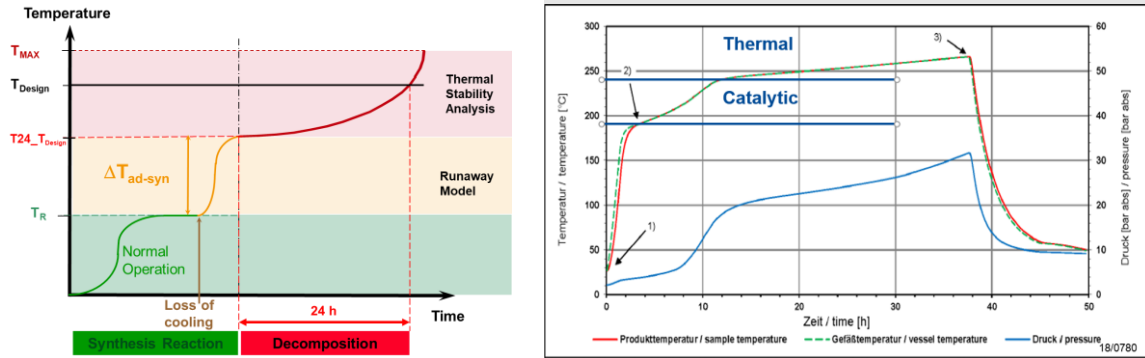


Figure 1. Left: Modified scenario of a cooling failure and T24 concept as used in the BASF's batch alkoxylation safety concept. Right: Adiabatic measurement of a polyetherol based on glycerine with approximately 9 PO units and high catalyst concentration

T24 values are derived from calorimetric techniques, such as differential scanning calorimetry (DSC), calvet calorimetry or adiabatic calorimetry (heat accumulation pressure vessel test). The most precise value is obtained from adiabatic calorimetry with high sensitivity and low phi-factor. Descriptions of the test methods and further references are available in R003e "Safety Characteristics" (BG RCI, 2016). Depending on the catalyst concentration and the degree of alkoxylation (i.e., molecular weight), the thermal stability varies significantly. An important observation from the measurements is the two-step decomposition of alkaline polyetherols. The first step seems to be induced by the catalyst and is therefore called "catalytic decomposition". It is directly correlated to the catalyst concentration. Usually, it has to be taken into account at temperatures of approximately 200°C. The second step occurs also without the presence of catalyst and is therefore called "thermal decomposition". Usually, it is observed in DSC measurements at temperatures above 300°C. Both steps can be recognized and discriminated in adiabatic measurements as indicated in Figure 1 (right). The thermal decomposition may become relevant at temperatures far below the DSC onset temperature. Besides the hazards resulting from the scenario of a cooling failure, a potential gas phase explosion may have severe effects. The highest risk arises from the decomposition of EO. It may decompose also in absence of oxygen, there is no upper explosion limit. From a viewpoint of explosion protection, the measures "avoidance of explosive atmosphere" and "avoidance of ignition sources" is suitable to prevent a gas phase explosion. Another measure is the explosion resistant design which is not suitable because of the high pressure increase factors during EO decomposition (Pekalski, et al., 2005). The first measure, "avoidance of explosive atmosphere" is implemented at BASF by using an empirical equation which is called Fath-equation. Given a partial pressure of nitrogen, this empiric model quantifies an upper pressure limit p_{Fath} (and hence limits the allowed partial pressure of EO) which guarantees that the concentration of gaseous EO is below the limiting stability concentration (self-decomposition) throughout the whole process. It results from measurements with EO/air/N₂-mixtures by varying composition, temperature and pressure.

4. Controlling the hazards

With knowledge of the amount of accumulated free oxide (chapter 2) as well as safe limits regarding temperature (T24) and pressure (p_{PSV} or p_{Fath}) (chapter 3), the missing piece that connects the current process conditions to the safe limits is a runaway model. Within the runaway model, the amount of free, accumulated oxide $n_{A,Acc}$, calculated from the current process pressure p and process temperature T (see chapter 3), defines the energetic potential which may be released in a runaway scenario. To determine if the reactor is in a safe state, a runaway reaction is simulated to quantify its consequences in case of, e.g., a power loss or insufficient cooling. During that runaway, the process temperature increases with oxide conversion ξ and can be described as

$$T(\xi) = T + \int n_{A,Acc} \xi \frac{\Delta h_R}{c_p(T, \theta)} d\xi \quad (5)$$

where θ also is a function of the conversion ξ , $\theta = \theta(\xi)$.

Due to the high reactivity the runaway happens on short timescales and is modelled as adiabatic. The maximum temperature occurs at the end of the runaway (full conversion of free oxide, $\xi = 1$), hence

$$T_{max} = T(1) \quad (6)$$

Not only the temperature increases during a runaway, but also the pressure. In the early phase of a runaway, pressure increases due to the temperature increase. With increasing consumption of the free alkylene oxide during the runaway (conversion), pressure decreases again. Thus, the maximum pressure does not occur at the end of the runaway but during the runaway at conversion ξ^+ , which can be calculated as

$$p_{max} = p(\xi^+) \quad (7)$$

$$p(\xi) = \sum p_i(T(\xi), \theta) \quad (8)$$

$$\frac{\partial p(\xi^+)}{\partial \xi} = 0 \wedge \frac{\partial^2 p(\xi^+)}{\partial \xi^2} < 0 \quad (9)$$

According to Eq(8), the pressure increase depends strongly on the amount of nitrogen and of other volatile constituents in the reactor (e.g., water or the starter material). Eq(8) can be solved analogously to Eq(1) and Eq(2) as described in chapter 2. Conservativeness of this equilibrium model to determine the maximum pressure during a runaway has been validated in lab trials.

Uncertainties of the model inputs must be considered and quantified as uncertainty margins. Error margins to be considered stem from sensor accuracies (e.g., temperature, pressure and mass flow) and property data uncertainties. Within a sensitivity analysis, which is carried out online, the aggregated uncertainty margins, $\Delta_\epsilon T$ and $\Delta_\epsilon p$, are determined for the maximum temperature and pressure expected respectively in the runaway scenario.

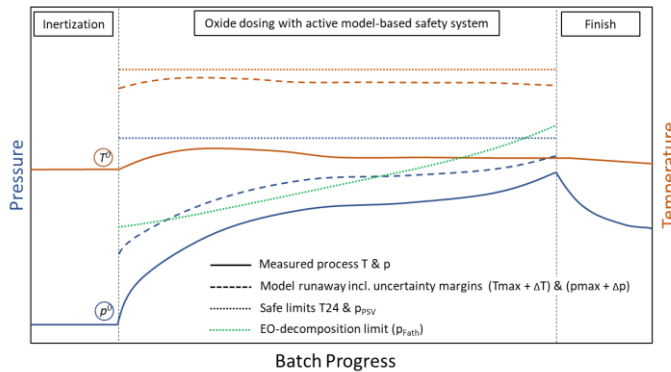


Figure 2: Sketch of a typical process temperature and pressure trend for semi-batch alkoxylation along with maximum temperatures and pressures of an online runaway model.

With the knowledge of the expected maximum temperature T_{max} and maximum pressure p_{max} (including the respective safety margins $\Delta_\epsilon T$ and $\Delta_\epsilon p$) as well as of the EO decomposition limit p_{Fath} , it can be evaluated if the reactor is in a safe state (given the current process pressure p and temperature T) by fulfilling the following three conditions:

$$p \leq p_{Fath} \wedge T_{max} + \Delta_\epsilon T \leq T24 \leq T_{Design} \wedge p_{max} + \Delta_\epsilon p \leq p_{PSV} \quad (10)$$

Violation of the condition defined by Eq(10) must trigger automated fallback to fail safe positions for all valves, most importantly shutting down any potential energy source like oxide dosage or any form of heating.

Figure 2 illustrates this evaluation of fulfillment of the three conditions given in Eq(10). The solid lines indicate current process conditions. Based on these process conditions, the amount of accumulated, unreacted alkylene oxide is calculated. The dashed lines then indicate the maximum temperature and pressure respectively, according to the described runaway model. The dotted lines illustrate the safety limits that may not be exceeded in case of a runaway and the EO decomposition pressures according to the Fath-Equation. An intersection of dashed lines and the matching dotted lines would indicate an impermissible accumulation of unreacted oxide as the design parameters of the reactor might be exceeded in case of a runaway and a potential subsequent

thermal decomposition. In that case, the alkylene oxide feed must be stopped. Alternatively, to an online evaluation of the hazardous potential of unreacted free oxide using current process pressures and temperatures, model calculations can as well be performed a priori. Using a predefined set of conservative boundary conditions with regards to the inertization conditions, process temperature and batch size (all safeguarded in the SIS), maximum allowed process pressures can be derived applying the same set of equations as within the online model. Those maximum process pressures limit oxide accumulations to fulfill the necessary conditions for a safe process. Important criterion for applying a pressure-based safety model is homogeneous mixing of the reaction mixture to ensure equilibrium. Thermodynamic equilibrium during oxide dosing is an adequate assumption which has been validated through lab trials, advanced process simulation and comparison with process data.

5. Conclusion

Herein, the most severe risks of alkoxylation reactions are presented. Although the risks itself are well known in literature, especially the combination thereof (e.g., a thermal runaway of unreacted accumulated alkylene oxide leading to a thermal decomposition) cannot be emphasized enough. The risks of a thermal runaway and thereby triggering of a subsequent thermal decomposition can not be mitigated by, e.g., a PSV. Instead, the presented and globally successfully applied model-based safety concept directly limits the core risk of the alkoxylation process: the amount of accumulated free oxide. Furthermore, by not relying on a PSV while unreacted alkylene oxide is present in the reactor, any risk of a release of alkylene oxide is inherently mitigated as well.

The model-based safety concept is based on the combination of an online measurement of pressure and temperature and a thermodynamic model, implemented in the safety instrumented system (SIS). The model determines the consequences of a thermal runaway (most importantly the maximum temperature) and compares it with the maximal allowed temperature (T24) to prevent the exceedance of the reactor's design temperature within 24 hours after the runaway due to the exothermal decomposition. Detailed knowledge of all relevant substance properties including starter materials, intermediates and products is crucial. Onset temperatures and decomposition kinetics should be thoroughly investigated with the catalyst present, as the catalyst is known to also catalyze decomposition reactions. Not only the risk of decomposition in the liquid phase, but also the risk of decomposition in the gas phase needs to be mitigated. Precise analytical data needs to be collected as basis for the model. Measurement uncertainty and sensor accuracies need to be considered in a conservative manner.

References

- BG Chemie, 2007. *M045, Ethylenoxid/Propylenoxid*. Heidelberg: Jedermann-Verlag.
- BG RCI, 2016. *R003e, Safety Characteristics, Measurement and Evaluation. DGVU Information 213-066*. Heidelberg: Jedermann-Verlag.
- BG RCI, 2022. *R 009, Reaktionen mit Ethylenoxid und andere Alkoxylierungen*. Heidelberg: Jedermann-Verlag.
- Ebel, H., Weid, C. & Hopwood, M., 2020. *Chemical explosion at IQOXE in Tarragona - Incident Investigation Report*. Hamburg: DNV GL Oil & Gas Germany.
- Gross, J. & Sadowski, G., 2001. Modeling Polymer Systems Using the Perturbed-Chain Statistical Associating Fluid Theory Equation of State. *Ind Eng Chem Res*, September, Volume 41, p. 1084–1093.
- Gygax, R., 1988. Chemical reaction engineering for safety. *Chem Eng Sci*, Volume 43, p. 1759–1771.
- Ionescu, M., 2016. *Chemistry and Technology of polyols for polyurethanes*. 2 ed. Shawbury, Shrewsbury, Shropshire: Smithers Rapra Technology Ltd..
- Maestri, F. & Rota, R., 2017. Simple Monitoring of Semibatch Polymerization Processes: An Integrated Criterion. *Ind. Eng. Chem. Res.*, 56(26), pp. 7434 - 7444.
- Neyraval, P., Egan, S. M., Basco, J. & Arques, J. S., 2022. Explosion of 14th January 2020 at IQOXE, Tarragona, Spain. *Chemical Engineering Transactions*, May, Volume 90, pp. 649-654.
- Pekalski, A. A. et al., 2005. Explosive decomposition of ethylene oxide at elevated condition: effect of ignition energy, nitrogen dilution, and turbulence. *J. Hazard. Mater.*, February, Volume 118, p. 19–34.
- Salg, S. & Lötgering-Lin, O., 2022. *Batch Alkoxylation Safety - Reactions with EO and other alkoxylation*. Antwerp, European Conference on Plant & Process Safety 2022.
- Salzano, E., Serio, M. D. & Santacesaria, E., 2007. The evaluation of risks of ethoxylation reactors. *Process Saf Prog*, Volume 26, p. 304–311.
- TRAS 410, 2012. *Technische Regel für Anlagensicherheit TRAS 410 - Erkennen und Beherrschen exothermer chemischer Reaktionen*. Berlin: Bundesministerium für Umwelt, Naturschutz und nukleare Sicherheit.