

## Reference Document

### Hazards of alkoxylation and measures to control them

Semi-Batch alkoxylation bears several risks. First, short chain epoxides like ethylene oxide (EO) or propylene oxide (PO) are toxic and shall not be released to the environment. Second, in case of a cooling loss during an alkoxylation reaction, accumulated free epoxide may lead to a thermal runaway of the synthesis reaction in which the pressure and, most notably, the temperature increases significantly. Third, if the temperature after the runaway is too high, a decomposition of the polyol can be triggered, which leads to further increase of temperature and pressure. Finally, if the epoxide concentration in the gas phase exceeds specific thresholds, explosive gas phase decomposition reactions might be triggered. In case of EO, gas phase decomposition is extra challenging since EO is chemically unstable and may decompose also in absence of oxygen. Mixed with air the explosion is even more severe.

The hazards arising from alkoxylation may be safeguarded by monitoring the free epoxide concentration throughout the whole process in sufficient quality. This value is not directly accessible but can be calculated from pressure measurement by knowing all ingredients and precise phase equilibria as well as property data for all compositions of the whole process. All relevant physical and chemical properties such as vapor pressure, density, heat capacity, solubility need to be determined in high quality and the measurement uncertainty needs to be considered. Sensor accuracies of the production equipment need to be considered as well.

A basic principle for safe production is the limitation of free unreacted oxide such that design limits are not exceeded in case of a runaway during the synthesis reaction. With regards to pressure, the design limit is the opening pressure of a safety valve, which should not be triggered during the runaway of the synthesis reaction. In this way, toxic epoxides can be contained and not released to the environment. With regards to temperature, the design limit is the reactor design temperature or the adiabatic decomposition temperature for an adiabatic induction time of 24 hours (ADT24), whatever value is smaller. When the ADT24 is reached, thermal explosion will occur after 24 hours at ideally adiabatic conditions. This temperature is set as maximum permissible temperature during or after a runaway. When this temperature is reached, additional countermeasures must be taken to return to safe conditions and to avoid the thermal explosion of the reactor.

The ADT24 can be derived from thermal analyses such as differential scanning calorimetry or adiabatic calorimetry. All process phases need to be considered and the thermal stability of raw materials including catalysts, intermediates and final products needs to be known. The

most instable composition should be taken as a representative for the determination of the ADT24. The decomposition temperature in DSC measurements is about 330 °C for neutral alkoxylates. At acid or basic conditions, the DSC onset temperature drops significantly, even below 200 °C in some cases. The decomposition energy is about 900 J/g. Depending on the catalyst concentration and the composition of the reaction mixture, ADT24-values in the range of 200 °C until 250 °C are typical, in some cases the ADT24 is even smaller than 200 °C. During the decomposition of the reaction mixture, flammable gases can be released. This should be considered for the design of exhaust or pressure relief systems.

For the prevention of a gas phase decomposition, the explosive range of all flammable components in the process needs to be known. The most hazardous component in these terms is ethylene oxide, usually, since it is chemically unstable. All influencing parameters such as temperature and pressure need to be considered for the determination of the explosive range. Note, that the limiting stability concentration decreases with increasing temperature and pressure.

A mode of operation outside the explosive range can be ensured by sufficient inertization with inert gases like nitrogen and a corresponding maximum permissible amount of epoxide in the gas phase. Particularly, the partial pressure of inert gas, vapor pressure of reactive or volatile components and the solubility needs to be known in all process phases for the correct calculation of the partial pressure of epoxide in the gas phase.

This document offers additional information and recommendations for the safe operation of alkoxylation processes. It may be incomplete and it is explicitly no comprehensive treatise about all potential hazards which may arise. Furthermore, concrete measures depend on individual safety concepts and equipment. The authors or BASF can not be held liable for the use of this document.