

Batch Alkoxylation Safety Reactions with EO and other alkoxylations

Dr. Steffen Salg BASF SE, Ludwigshafen, Germany

European Conference on Plant & Process Safety 2022 13 & 14 September 2022, Antwerp, Belgium

Alkoxylation – chemistry and hazards



Main hazards to be safeguarded

- Runaway of synthesis reaction / accumulation of alkylene oxide
- Decomposition of raw materials, intermediates and products (liquid and gaseous)
- EO decomposition also in absence of oxygen
- Flammable and toxic gases (EO and decomposition gases)



Examples of incidents with alkoxylation reactions



BASF Polyol Plant, Geismar, USA Mai 24, 1976

Runaway with subsequent thermal decomposition



IQOXE EO & derivatives plant, Tarragona, Spain - January 14, 2020

Under investigation



Alkoxylation – chemistry and hazards



Main hazards to be safeguarded

- Runaway of synthesis reaction / accumulation of alkylene oxide
- Decomposition of raw materials, intermediates and products (liquid and gaseous)
- EO decomposition also in absence of oxygen
- Flammable and toxic gases (EO and decomposition gases)



Controlling the runaway and exothermic decomposition

Derivation of maximum allowed temperature (after runaway) according to the scenario of a cooling failure by Gygax and recommendations of TRAS 410¹



Gygax, R., *Chemical reaction engineering for safety,* Chemical Engineering Science, 1988. **43**(8): p. 1759-1771.

| Reaction temperature |
|--|
| Maximum temperature of the synthesis reaction |
| Adiabatic temperature rise |
| Time to maximum rate at adiabatic conditions |
| Adiabatic decomposition temperature for an adiabatic induction time of 24 hours = Temperature, at which the TMR equals 24 h = Limiting factor in the safety model |
| |

¹Technische Regel für Anlagensicherheit 410



Thermal stability of polyether polyols Methods for quantitative assessment

Calorimetric methods for the study of decomposition reactions and determination of the **ADT24**

- Differential Scanning Calorimetry (DSC)
- Calvet calorimetry
- Adiabatic calorimetry *preferred option*
- Use of a formal kinetic model describing the decomposition reaction





Thermal stability of polyether polyols Two-step decomposition at alkaline conditions



- The most precise assessment is possible by adiabatic calorimetry
- Derivation of the ADT24 which is used as a limiting factor in the safety model





Thermal stability of polyether polyols Characteristics of the decomposition reaction

- Decomposition energy of polyether polyols ~= 900 J/g
- ADT24 ~= 200 °C 250 °C, in some cases even smaller than 200 °C
- In alkaline conditions, decomposition may become more severe and may present autocatalytic behavior
- ADT24 needs to be determined for the most instable composition (raw materials including catalysts, intermediates or final products)
- **Prevention**: Maximum temperature of synthesis reaction MTSR ≤ ADT24 in combination with additional countermeasures
- Effective countermeasures depend on process design and include for example emergency cooling, ambient cooling, drainage systems
- Pressure relief is not sufficient as thermal decomposition may continue despite gas removal
- Decomposition leads to formation of flammable gases (additional risk, relevant e. g. for pressure relief)

Alkoxylation – chemistry and hazards



Main hazards to be safeguarded

- Runaway of synthesis reaction / accumulation of alkylene oxide
- Decomposition of raw materials, intermediates and products (liquid and gaseous)
- EO decomposition also in absence of oxygen
- Flammable and toxic gases (EO and decomposition gases)



Gas phase decomposition of alkylene oxide

- Gas phase: potentially ignitable alkylene oxide-oxygen-mixture
- Low oxygen content in the reactor due to vacuum before inerting with N₂
 - PO/BuO-O₂-mixtures out of the explosive range at typical process conditions
 - EO-O₂-mixture: hazard of exceeding the limiting stability concentration (LSC)
- Specification of the maximum permissible partial pressure EO
- Protection against gas phase decomposition of EO by Fathequation:

 $p_{Fath} = f(p_{N_2}, T, \dots)$

10 LSC 90 20 No UEL 30 40 Fuel Inert gas 50 in Mol-% in Mol-% 60 **Decomposition** 40 .70 30 Explosive range 80 LEL 90 Combustion 100 80 50 40 30 20 90 60 10 100 Air in Mol-%

Askar, E.: Experimentelle Bestimmung und Berechnung sicherheitstechnischer Kenngrößen ethylenoxidhaltiger Gasphasen, BAM Berlin, 2012



PO: propylene oxide BuO: butylene oxide

EO: ethylene oxide

Alkoxylation – chemistry and hazards





Safeguarding semi-batch reactors for alkoxylation Components



Semi-batch process: pre-charge of raw materials and dosage of alkylene oxide

Components

- Starter
- Catalyst
- Oxide
- Solvents
- Oxide types
- Ethylene Oxide (EO)
- Propylene Oxide (PO)
- Butylene Oxide (BO)



Safeguarding semi-batch reactors for alkoxylation Challenges



Non-Steady Process

Variables:

fill level

composition

pressure

temperature

nitrogen initial pressure

process steps

thermal stability

. . .









Hazardous potential

- ✓ Toxicity of the oxides
- ✓ Runaway reaction
- Exothermic decomposition (ADT24)
 - Gas phase decomposition





Hazardous potential

- ✓ Toxicity of the oxides
- ✓ Runaway reaction
- Exothermic decomposition (ADT24)
- ✓ Gas phase decomposition



Calculation of oxide accumulation during alkoxylation processes





Calculation of oxide accumulation during alkoxylation processes



Ne create chemistry

19 13.09.2022 Salg, BASF SE

Summary – key factors of BASF's model-based safety concept

- Ensure that reaction is running with sufficient reaction rate
 - > Minimum reaction temperature, sufficient mixing, catalyst quality
- Limitation of oxide accumulation to control potential runaway + subsequent decomposition of liquid phase as well as EO decomposition
 - Maximum temperature of synthesis reaction MTSR < ADT24</p>
 - Sufficient inertization, e.g. N₂
 - EO amount < limiting stability concentration</p>
- Use of precise property & thermal stability data as well as correct description of vapor-liquid-equilibrium (VLE) in all phases of the process, respecting changes in composition of the reaction mixture
- Consideration of accuracy of sensors and measurement uncertainty
- Stable process design (prevention of oscillations)
- Proper design of pressure relief considering release of flammable gases / containment of toxic gases
- Sufficient quality/redundancy of SIL-functions according to risk matrix
- Use of a MOC system and risk analysis for changes in process or equipment



Acknowledgement

Various BASF colleagues contributed to this work:

- A. Brodhagen sponsor & chair
- S. Salg technical lead
- W. Sager
- R. Ries
- E. Escriba Aguila
- M. Gödde
- O. Lötgering-Lin
- C. König
- T. Heitz



BASE We create chemistry