

Case History 03 : « DMSO »

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Dimethyl-sulfoxide (DMSO) is an aprotic polar solvent often used in organic chemical synthesis. It is known for its limited thermal stability and usually precautions are taken to avoid its exothermal decomposition. The decomposition energy is approximately $500 \text{ J} \cdot \text{g}^{-1}$, which corresponds to an adiabatic temperature rise of over 250 K.

This solvent was used for a synthesis during a campaign in a pilot plant. It was known that it was contaminated with an alkyl bromide. Thus it was submitted to a chemical and thermal analysis, which allowed defining safe conditions for its recovery, i.e. a maximum heating medium temperature of 130 °C for a batch distillation under vacuum. These conditions were established in order to ensure as well the required quality and a safe operation. A second campaign, which was initially planned, was delayed and in the mean time the solvent was stored in drums.

One year later, the DMSO was needed again in the pilot plant and it was decided to proceed with the distillation for recovering a pure solvent. As vacuum was applied to the stirred vessel (4 m³), difficulties occurred to reach the desired vacuum. Thus the operators were looking for a leak in the system until somebody noticed a sulphide like smell at the vacuum pump exhaust. It was decided to change the vacuum pump oil that was supposed to be contaminated. For doing so, the distillation flap was closed, insulating the vessel from the distillation system, which was brought to atmospheric pressure for allowing the oil to be changed. After thirty minutes, the vessel exploded causing important material damage and one operator was injured by flying debris.

What the incident analysis revealed:

- The thermal analysis was repeated on the stored raw DMSO as it was before distillation. The thermal stability was shown to have strongly decreased, when compared to the analysis performed before storage.
- DMSO decomposes following an autocatalytic behaviour. During storage decomposition products that catalyse the decomposition were slowly formed. Consequently the induction time of the decomposition decreased such that only thirty minutes were left at 130 °C.

Lessons learned:

Even a very slow decomposition may impinge the thermal stability of a substance decomposing by an autocatalytic mechanism. Thus the time factor plays an important role.

Thermal analysis should always be performed on samples that are really representative for the substance to be processed.

To prepare the presentation, use the information in the Bretherick on DMSO (Bretherick: see book reference on moodle). Briefly describe what an autocatalytic decomposition is.

