

THERMAL HAZARDS AND SAFE SCALE-UP OF REACTIONS CONTAINING DIMETHYL SULFOXIDE

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Extensive thermal analysis has shown that DMSO-containing reaction mixtures can be more energetic and decompose at lower temperatures than pure DMSO. Several processes at Merck using DMSO as a solvent were found to have the onset temperatures of decompositions reduced to the point where it became a thermal and operational hazard. The onset temperature depended on the reagents in the reaction mixture and the thermal history of the mixture. The case studies presented in this paper will include discussion on what process hazards were identified, how the process hazards differ from the pure DMSO hazards, and how to scale up these processes safely.

Keywords: ARC, decomposition, dimethyl sulfoxide, DMSO, exothermic, thermal hazard

Introduction

Dimethyl sulfoxide, DMSO, is commonly used as a solvent in many chemical reactions due to its capability to solubilize many inorganic and organic compounds. However, despite of its common use, there have been several serious incidents associated with DMSO reported in the literature both at the laboratory scale and at the industrial scale.

Hall [1] reported a fatal incident in a laboratory in 1991, where DMSO was inadvertently contacted with traces of perchloric acid which resulted in an explosion, fatally injured the technician. The laboratory damage exceeded 60000 German marks. A pilot plant reactor exploded in 1991 [1] during a vacuum distillation of a DMSO mixture containing 5% of 2-bromo-methyl-1,3-dioxolane and 7% water. An investigation of the incident indicated that ~0.3% hydrogen bromide (HBr) was found to form during the long-term storage of the mixture. It is believed that HBr catalyzed the DMSO degradation at elevated temperatures, which was then accelerated by its decomposition product, dimethyl sulfide, resulting in rapid temperature and pressure rises. The explosion destroyed the reactor with the reactor cap being blown through several levels of the pilot plant and the reactor body propelled from the first floor to the ground level. The structure damages were over half of a million dollars. Bromides catalyzed DMSO decomposition is known and documented in 'Bretherick's Handbook of Reactive Chemical Hazards' [2]. Other incidents related to DMSO can be found in [1, 2].

Unlike most solvents, DMSO is very reactive and undergoes a violent exothermic decomposition just

above its atmospheric boiling point. Reaction mixtures containing DMSO can be much more hazardous than the pure solvent as the DMSO decomposition can become more violent. Several processes at Merck using DMSO as a solvent were found to have the onset temperatures of decompositions reduced to the point where it became a thermal and operational hazard. The onset temperature depended on the reagents in the reaction mixture and the thermal history of the mixture. Due to variation of the onset temperatures and the violent decomposition, processes using DMSO need to be evaluated carefully to ensure their safe scale-up. The case studies presented in this paper will include discussion on what process hazards were identified, how the process hazards differ from the pure DMSO hazards, and how to scale up these processes safely.

Experimental

Various thermal analytical tools were used to assess thermal hazards of processes. These include differential scanning calorimetry (DSC) [3], reactive system screening tool (RSST) [4] and accelerating rate calorimetry (ARC) [5]. The DSC runs were scanned at 5°C min⁻¹ from room temperature to ~300°C under a nitrogen atmosphere in a tantalum-lined crucible, which can withstand a pressure of approximately 500 psi. The sample mass in each DSC run was about 5 mg. Detail description on the in-house developed crucible can be found in [6]. The experimental parameters of ARC runs are summarized in Table 3.

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