Question 76: What can cause exothermic reactions in propylene driers and guard beds and how can these reactions be prevented?

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As introduction, Propylene Recovery Units downstream of FCC units typically consist of a C3/C4 Splitter, a Deethanizer and a C3 Splitter in series. The propylene from the C3 Splitter overhead is treated in regenerable molecular sieve Driers for moisture removal and finally passed through Guard Beds for trace contaminant removal. The principle trace contaminants being removed by the guard beds are carbonyl sulfide, arsine and phosphine. There are a variety of guard bed adsorbents that are used. Metal oxide bound on an alumina support is one type of adsorbent often used for trace contaminant removal. Occasionally hybrid type adsorbents are utilized (downstream of the driers) to remove trace levels of oxygenates, organic sulfur species and nitrogen compounds.

With regard to the molecular sieve driers, there is a small (10-15°F) adsorption exotherm when liquid propylene is first charged to the molecular sieve adsorbent. This small exotherm dissipates quickly as propylene flows through the drier beds. Exothermic runaways are unlikely on molecular sieve type moisture driers operating normally to remove dissolved moisture from liquid phase propylene. Elevated levels of diolefins, oxygenates or metals could potentially cause exotherms in the molecular sieve drier.

During start-up and operation of any adsorption system it is important to stay within the pressure and temperature limits set by the equipment and adsorbent manufacturers. Excessive temperatures can cause equipment failure and result in life-threatening fire or explosion. There are a number of factors that can cause excessive temperatures in adsorbent systems.

1. Introducing a flammable or reactive fluid into a vessel containing air.

2. Introducing a high concentration of a reactive, strongly adsorbed material into fresh or regenerated adsorbent. In applications where there is sufficiently high risk of thermal excursions a low reactivity adsorbent should be considered.

3. Using a highly reactive fluid to heat or cool the bed. Examples of reactive fluids would include ethylene, propylene and other olefins.

As mentioned above, when equipment and adsorbent operating guidelines are followed closely, there is normally a small adsorption exotherm during initial commissioning and this exotherm dissipates quickly as propylene flows through the drier beds.

There have been two incidents of uncontrolled exotherms occurring in FCC PRU adsorption beds.

1. In one case an operator changed the temperature permissive from 122°F to 338°F (50°C to 170°C) in the drier regeneration control system, allowing excessively hot propylene from the freshly regenerated drier vessel to enter the lead COS/Arsine guard bed vessel. The high temperature propylene initiated

highly exothermic auto-reduction of the metal oxide to the elemental metal through both guard beds in series. The exotherm caused the paint to blister on the vessels and piping and the guard bed adsorbent was fused, but the system did not lose containment.

2. The second incident was more serious in that the vessel (containing stacked beds of two different adsorbents) lost containment. The vessel operated up flow. The inlet section of the adsorbent bed contained an adsorbent for removal of moisture and trace oxygenates. The exit section of the adsorbent bed contained adsorbent selective for the removal of COS. The investigation of this incident identified vapor phase propylene (instead of liquid phase propylene) being sent to the vessel for 67 minutes, with concomitant bed channeling, high heat of adsorption in the inlet section (where a reactive adsorbent was installed) and poor heat dissipation as the root cause of the failure. High local temperature and stresses exceeding the tensile strength of the vessel shell led to rupture of the shell near the end of the inlet section of adsorbent.

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Propylene is a reactive fluid and therefore a known exothermic reaction is propylene polymerization which can be catalyzed by the adsorbent material. Typically, these reactions are not significant and are not observed if the adsorbent material is proper for propylene use and the heat of adsorption during startup is adequately dissipated. At higher temperatures these reactions can accelerate rapidly.

Within our network there have been few reports of incidents involving propylene driers and the investigations of these events have not identified common root causes. Learning’s from these events include ensuring the proper adsorbent material is selected and that startup procedures include temperature increase limits with corrected actions if exceeded.

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