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Messages for Manufacturing Personnel

Can overcooling a reactor cause a runaway reaction?

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In 1996, there was an explosion of a 600 US gallon (~2.3 cu m) batch reactor in a British dye factory. The process required addition of nitrosyl sulfuric acid (NSA) to the reactor, containing an amine and sulfuric acid, at a temperature between 30 and 40 °C. The reaction was exothermic – it generated heat. The feed typically took about 5 hours, and the feed was manually controlled. This process had been operating for many years, and hundreds of batches prepared without problem.

Early in the NSA feed, the batch was overheated to almost 50 °C and the NSA feed was stopped. The batch was then cooled to 25 °C (too cold) and NSA addition was resumed. When the NSA feed was completed the batch temperature could not be controlled with the available cooling, and exceeded the maximum temperature which could be recorded by the temperature instrument. The reactor was overpressurized by the runaway reaction and it exploded. The lower part of the reactor was propelled off of its supports onto the building floor. The reactor agitator landed on the roof, and the top of the reactor was found about 500 ft (150 m) away. Fortunately, nobody was injured. The direct cost was more than 2 million UK Pounds.

Reference: Partington and Waldram, *IChemE Symposium Series*, No. 148, pp. 81-93, 2001.

Damage from other runaway reactions

Jacksonville, Florida, 2007

Morganton, North Carolina, 2006

Did you know?

- The rate of most exothermic chemical reactions increases as the temperature increases, and decreases at lower temperature. If the reaction temperature is too low, the reaction will be slower, and unreacted material may accumulate in the reactor. If the reaction temperature then increases, the unreacted material will be available to react. If there is enough unreacted material, the energy released may exceed the reactor cooling capacity.
- At high temperature, other chemical reactions including decomposition reactions which are not important at the intended reaction temperature may become significant. These reactions may release more energy, and the reaction products might include gases which can generate high pressure in a reactor.
- In this incident, it is believed that approximately 30% unreacted NSA accumulated in the reactor during the time that the batch was too cold. Laboratory studies and computer simulations indicated that this accumulation might not have been sufficient to cause the runaway. Another heat source, such as a steam leak to the reactor jacket, might have been necessary. However, the energy available from unreacted NSA made the reactor more vulnerable to a runaway if there were other heat sources.
- It is important to ensure that reaction systems are in good working order, since equipment leaks and other malfunctions can cause, or contribute to, chemical reaction incidents.

What can you do?

- Know which of your reactions are exothermic, and may become uncontrollable if reactants accumulate. Some examples include polymerization, nitration, sulfonation, acid-base reaction, and oxidation.
- Be aware that, for many reactions, it is not only the upper temperature limit which is critical for safety, but also the lower temperature limit. Overcooling a reactor can result in accumulation of unreacted material which can cause an uncontrollably high temperature later.
- Understand the consequences of deviating from critical safety parameters – temperature, pressure, flow rate, mixing, or whatever is critical for your process. Be aware of the consequences of deviations, both too high and too low, and know what action to take if a deviation occurs.
- If you do not have chemical reaction processes in your plant, be aware that low temperature can still cause problems. For example, liquids may freeze or become very thick, or solids may precipitate out of a solution.

It might not be safe if your process is "too cool"!

Questions:

Students may find helpful the Rules for Safe Operation of Batch Reactors section in this resource.

1. **(10 min)** What main mistake did the operators make? Discuss the ramifications of the mistake. Consider important the following aspect of the disaster that the article did not address: the heating of the batch to 50 C. What effect did this one action have on the contents of the reactor? What should the operators have done immediately after the batch was heated to 50 C?.
2. ***(20-30 min)** After the batch contents were at 25 C, what course of action could have prevented this runaway reaction from occurring? How could this batch have been saved so it converted to desired products as intended? (*Hint:* Consider whether or not the batch contains a high undesired product composition.)
3. **(5 min)** lessons have you learned from this article about initial overheating, over-cooling, and batch size and how can you apply this to your chemical engineering career?