ChE 344 Reaction Engineering and Design

Safety Module 2a: Monsanto Runaway Reaction†

This module is based on Example 13-2 in the 2nd edition of Essentials of Chemical Reaction Engineering and the 5th edition of Elements of Chemical Reaction Engineering.

Problem Statement: A serious accident occurred at the Monsanto plant in Sauget, Illinois, on August 8, 1969 at 12:18 AM. (see Figure E13-2.1). (Sauget (pop. 200) is the home of the 1988 Mon-Clar League Softball Champions.) The blast was heard as far as 10 miles away in Belleville, Illinois, where people were awakened from their sleep. The explosion occurred in a batch reactor that was used to produce nitroaniline and ammonium chloride from ammonia and o-nitrochlorobenzene (ONCB):

\[
\begin{align*}
\begin{array}{c}
\text{NO}_2 \ \text{Cl} \\
\text{Cl}
\end{array}
+ 2\text{NH}_3 & \rightarrow \\
\begin{array}{c}
\text{NO}_2 \\
\text{NH}_2
\end{array}
+ \text{NH}_4\text{Cl}
\end{align*}
\]

This reaction is normally carried out isothermally at 175°C and about 500 psi. The ambient temperature of the cooling water in the heat exchanger is 25°C. By adjusting the coolant rate, the reactor temperature could be maintained at 175°C. At the maximum coolant rate, the ambient temperature is 25°C throughout the heat exchanger. Let me tell you something about the operation of this reactor. Over the years, the heat exchanger would fail from time to time, but the technicians would be “Johnny on the Spot” and run out and get it up and running within 10 minutes or so, and there was never any problem. It is believed that one day someone in management looked at the reactor and said, “It looks as if your reactor is only a third full and you still have room to add more reactants and to make more product and more money. How about filling it up to the top so we could triple production?” They did, and started the reactor up at 9:45 PM. As before, the heat exchanger went down at 10:30 PM. The reaction continued until around midnight when the reactor exploded. The aftermath is shown in the following figure.

Figure E13-2.1. Aftermath of the explosion. (St. Louis Globe/Democrat photo by Roy Cook. Courtesy of St. Louis Mercantile Library.)

† Adapted from the problem by Ronald Willey, Seminar on a Nitroaniline Reactor Rupture. Prepared for SACHE, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York (1994). Also see Process Safety Progress, vol. 20, no. 2 (2001), pp. 123–129. The values of \(\Delta H_{Rx}\) and \(UA\) were estimated from the plant data of the temperature–time trajectory in the article by G. C. Vincent, Loss Prevention, 5, 46–52.
The model equations and parameter values are given in Example 13-2 of the textbook. One added note: As long as \( Q_g \) is less than the maximum value of \( Q_r \), a temperature controller can maintain the temperature at 175°C. Consequently, any temporary upset due to heat exchange failure where the temperature will be returned to 175°C provided the maximum value for \( Q_r \) is greater than \( Q_g \).

While a Chemical Safety Board video of incident does not exist for the Monsanto explosion, a parallel incident with similar circumstances and concepts (\( Q_g > Q_r \)) can be found in the Synthron Explosion. The Chemical Safety Board video can be helpful for understanding parallels between explosions, however, note that the situations are different, and the problems that follow are only regarding the Monsanto situation.

**Synthron Video:** ([https://www.youtube.com/watch?v=sRuz9bzBrY](https://www.youtube.com/watch?v=sRuz9bzBrY)) Note: Only relevant from 2:00-7:00


**Monsanto Runaway Power Point:** ([http://umich.edu/~safeche/assets/pdf/Ch9Explosion.ppt](http://umich.edu/~safeche/assets/pdf/Ch9Explosion.ppt))

*Note:* This PowerPoint also served as an introduction to Chemical Reaction Engineering, so only slides 1-15 are relevant for this module.

(a) It is important that chemical engineers have an understanding of what the accident was, why it happened and how it could have been prevented in order ensure similar accidents may be prevented. Applying a safety algorithm to the accident will help achieve this goal. In order to become familiar with a strategy for accident awareness and prevention, re-read the background information on the Monsanto explosion and fill out the following Safety Algorithm for the Monsanto incident. See definitions on the last page.

**Safety Analysis of Monsanto Incident**

| Activity: | ____________________________________________ |
| Hazard: | ____________________________________________ |
| Incident: | ____________________________________________ |
| Initiating Event: | ____________________________________________ |
| Preventative Actions and Safeguards: | ____________________________________________ |
| Contingency Plan/ Mitigating Actions: | ____________________________________________ |
Lessons Learned: ____________________________________________

For Parts (b) through (f), go to Living Example Problems in Chapter 13 of Elements or Essentials of Chemical Reaction Engineering and load Example 13-2 using Wolfram.

http://www.umich.edu/~elements/5e/tutorials/Wolfram_tutorials.html

You can download Wolfram on your computer for free, just follow the instructions at the bottom of the LEP web page (http://www.umich.edu/~elements/5e/13chap/live.html).

(b) Show the explosion would not have occurred if the ONCB amount had not been increased and the downtime and time the heat exchanger failed were the same, i.e., \( t_1 = 45 \) minutes and \( t_2 = 55 \) minutes.

(c) Show the explosion would not have occurred for the triple production cake if the heat exchanger had not failed.

(d) Question for consideration. Does it make any sense to plot the down time, \((t_2 - t_1)\), versus time since the start of the reaction that the reactor fails, \(t_1\) to identify regions where the explosion will and will not occur? Explain.

\[
\begin{array}{c|c|c}
\text{Explosion} & \text{t_2-t_1} & \text{No Explosion} \\
\hline
\text{Explosion} & \text{t_1} & \text{No Explosion}
\end{array}
\]

If it does make sense please prepare such a plot, if not explain why. Hint: Choose \( t_1 \) and then find the largest \( t_2 \) for which the reaction will not run away. Choose another larger value of \( t_1 \) and repeat. Continue in this manner to construct your plot.

(e) Vary other Wolfram parameters and write a set of conclusions.

(f) Describe what was the most unsettling to you about these incidents.
Additional Information:

Rate law: \(-r_{\text{ONCB}} = kC_{\text{ONCB}}C_{\text{NH}_3}\)

With \(k = 0.00017 \text{ m}^3 \text{kmol}^{-1} \text{min}^{-1}\) at 188°C (461K) and \(E = 11.273 \text{ cal mol}^{-1}\)

The reaction volume for the new charge of 9.0448 kmol of ONCB:
\[ V = 3.265 \text{ m}^3 \text{ONCB/NH}_3 + 1.854 \text{ m}^3 \text{H}_2\text{O} = 5.119 \text{ m}^3 \]

The reaction volume for the previous charge of 3.17 kmol of ONCB:
\[ V = 3.26 \text{ m}^3 \]

\[ \Delta H_{\text{Rx}} = -5.9 \times 10^5 \frac{\text{ kcal}}{\text{ kmol}} \]

\[ C_{\text{PONCB}} = C_{\text{PA}} = 40 \frac{\text{ cal}}{\text{ mol} \cdot \text{K}} \]

\[ C_{\text{PH}_2\text{O}} = C_{\text{PW}} = 18 \frac{\text{ cal}}{\text{ mol} \cdot \text{K}} \]

\[ C_{\text{PNH}_3} = C_{\text{PB}} = 8.38 \frac{\text{ cal}}{\text{ mol} \cdot \text{K}} \]

Assume that \(\Delta C_p \approx 0\)

\[ UA = 35.85 \frac{\text{ kcal}}{\text{ min} \cdot ^\circ\text{C}} \text{ with } T_A = 298K \]

Definitions

Activity: The process or activity for which risk to people, property or the environment is being evaluated.

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property or the environment.

Incident: What happened? Description of the event or some of the events along with the steps that lead to one or more undesirable consequences, such as harm to people, damage to the property, to the environment, or asset/business losses.

Initiating Event: The event that triggers the incident, (e.g. failure of equipment, instrumentation, human actions, flammable release, etc.). Could also include precursor events, e.g. no flow from pump, valve closed, inadvertent human action, ignition. The root cause of the sum events in causing the incident.

Preventative Actions and Safeguards: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property or the environment. Brainstorm all problems that could go wrong and then actions that could be taken to prevent them from occurring.

Contingency Plan/ Mitigating Actions: These actions occur after the initiating event. They are steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring.