Process Safety Evaluation

University of Alberta, 16th November, 2011

Mark Smith, Process Safety Manager
Introduction

• Causes of Accidents
• Techniques for Process Safety Evaluations
• Electrostatic Hazards
• Process Safety Methodology
• Case Studies
(23) A batch of crude product was being recovered for the first time by a method devised as a scale-up of a laboratory technique. The heat transfer had not been properly considered. An exothermic decomposition of hydroxylamine occurred. The lid of the reactor and the stirrer were blown 50 feet through the roof of the building. The gear box was blown 250 feet and the body of the reactor dropped to the ground. There was extensive damage to buildings.

Barton, J., Rogers, R., Eds.; Chemical Reaction Hazards, 2nd ed; Gulf Publishing Company
Causes of Accidents (US Chemical Safety and Hazard Investigation Board – CSB)

Following review of 167 serious incidents analyzed by the CSB involving uncontrolled chemical reactivity from 1980 to 2001, there is a pattern of lack of understanding of:

- Rate and quantity of heat or gas generated
- Maximum operating temperature to avoid decomposition
- Thermal stability of reactants, reaction mixtures, by-products, waste streams, and products
- Effect of variables such as charging rates, catalyst addition, and possible contaminants
- Understanding the consequence of runaway reactions or toxic gas evolution

Causes of Accidents (2)

Of the 167 serious incidents analyzed by the CSB involving uncontrolled chemical reactivity from 1980 to 2001:

- 48 resulted in 108 fatalities
- On average, six injury-related incidents per year, resulting in five fatalities annually
- Over 40 different chemical classes identified
- 36% attributed to chemical incompatibility
- 35% to runaway reactions
- 10% to impact-sensitive, or thermally sensitive materials

Causes of Accidents (3)

Consequences of the reactive incidents:
- 42% resulted in fire and explosions
- 37% resulted in toxic gas emissions

Relating to equipment:
- 65% were accounted for by storage and process equipment (i.e., excluding reaction vessels)
- 25% chemical reaction vessels

Chemical Reaction Hazards: Scale-up

Designing and Operating Safe Chemical Reaction Processes (HSE; HSG143)

\[ k = Ae^{-E_a/RT} \]

Volume of sphere = \( \frac{4}{3} \pi r^3 \)

Surface area of sphere = \( 4 \pi r^2 \)
Chemical Reaction Hazards: Scale-up (2)

An illustration\(^{21}\) of the effect of heat transfer in relation to vessel size and geometry is to consider the time taken for a 1 degree drop in temperature to occur by natural cooling from an initial temperature of 80°C when the surroundings are at 20°C.

<table>
<thead>
<tr>
<th>Reactor Size</th>
<th>Time to Cool</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 m(^3) reactor</td>
<td>20 minutes</td>
</tr>
<tr>
<td>5 m(^3) reactor</td>
<td>40 minutes</td>
</tr>
<tr>
<td>12.7 m(^3) reactor</td>
<td>60 minutes</td>
</tr>
<tr>
<td>25 m(^3) reactor</td>
<td>230 minutes</td>
</tr>
<tr>
<td>10 ml test tube</td>
<td>10 seconds</td>
</tr>
<tr>
<td>100 ml glass beaker</td>
<td>20 seconds</td>
</tr>
<tr>
<td>1 l glass dewar</td>
<td>60 minutes</td>
</tr>
<tr>
<td>1 l stainless steel</td>
<td>250 minutes</td>
</tr>
</tbody>
</table>

Designing and Operating Safe Chemical Reaction Processes (HSE; HSG143)
Process Safety Evaluations

Critical Assessment of Chemical Processes:

- Desk Screening
- Thermal Screening
- Characterization of the Desired Reaction
- Characterization of the Undesired Reaction
Desk Screening

- Literature searches
- Bretherick’s Handbook of Reactive Chemical Hazards, Sax’s Dangerous Properties of Industrial Materials
- Desktop calculations such as Oxygen Balance and CHETAH calculations (ASTM Computer Program for Chemical Thermodynamic Energy Release Evaluation)
- Assessment of molecules for hazardous functional groups
Thermal Screening

Used primarily at the laboratory scale development stage and equipment options include: Differential Scanning Calorimetry (DSC), Carius Tube, TSU, RSD, Radex and Differential Thermal Analysis (DTA). Carius Tube, TSU, RSD and Radex provide pressure data.

These techniques can be used to examine the thermal stability of an individual reaction component or a reaction mixture. Other tests such as shock sensitivity may also be considered at this stage.
Characterization of the Desired Reaction

Usually isothermal calorimetry to give data on reaction heats, reaction kinetics, thermodynamics and heat transfer. Equipment includes the commercially available calorimeters from Mettler (RC1), HEL (Simular), Setaram (DRC) and Chemisens.

Instruments to quantify the gas evolution rate during the reaction include thermal mass flow meters, Ritter gas meters, and U-tube devices. For all gas measurement, the material of construction of the device and the solubility of the evolved gas in the instrument fluid should be considered.
Characterization of the Undesired Reaction

Usually performed using adiabatic calorimetry to gain runaway data on reactions and individual materials. This also then leads to data for reaction pressure relief sizing and other protective measures.

Commercial equipment includes ARC, Phi-TecII, APTAC, ARSST, VSP2 and adiabatic Dewar.
Tools/Techniques Used at Gilead Alberta

- Differential Scanning Calorimeter (DSC)
- Thermogravimetric Analysis (TGA)
- Rapid Screening Device (RSD)
- Reaction Calorimeter (RC1)
- Accelerating Rate Calorimeter (ARC)
- MiniFlash FLPL (flash point determination)
- Conductivity Meter (conductivity measurements)
Differential Scanning Calorimetry (DSC)
Example of DSC Thermogram (HOBt)

Method: HP Gold 25/350/5
25.0-350.0°C 5.00°C/min  N2, 50.0 ml/min

Integral  5929.28 mJ
normalized 2117.60 Jg^-1
Onset  194.72 °C
Peak  216.13 °C

Integral  -369.97 mJ
normalized -132.13 Jg^-1
Onset  156.21 °C
Peak  158.25 °C

Note: No weight loss recorded upon completion of test

Lab: Alberta

STAR® SW 10.00
DSC Thermogram of Intermediate

Integral: 9429.65 mJ
normalized: 1264.03 Jg^-1
Onset: 239.86 °C
Peak: 274.26 °C

Integral: -552.86 mJ
normalized: -74.41 Jg^-1
Onset: 74.11 °C
Peak: 75.45 °C

Note: No weight loss recorded upon completion of test.

Lab: Alberta

17.12.2007 09:21:15
Thermogravimetric Analysis (TGA)
Rapid Screening Device (RSD)
Example of RSD Chart
RC1 Reaction Calorimeter

Motor (agitation)

Reactors

Cooling Unit

Gas Flow Meter

Metering Pumps

Balances
Reaction Calorimeter (RC1) – Heat Flow Calculation

\[ Q_r = U \cdot A \cdot (T_r - T_j) \]

- **Q_r**: heat flow through the reactor wall \([\text{J/s = W}]\)
- **U**: overall heat transfer coefficient of the reactor wall \([\text{W/m}^2\text{K}]\)
- **A**: heat exchange area (wetted area) \([\text{m}^2]\)
- **T_r**: temperature of the reactor contents \(^[\circ\text{C}]\)
- **T_j**: jacket temperature \(^[\circ\text{C}]\)
Example of RC1 Data

Starter in DCM Addition
(scaled to 40 g of starting material)

Reaction mixture warmed to 22 °C over 60 minutes, to complete

Observed heat of reaction -92 kJ per mole of starting material, equivalent to an adiabatic temperature rise of about 31 K

Reaction performed in Tr mode, set point -10 °C

120 g of SM in DCM charged over two hours
RC1 Evaluations

- Heat of reaction
- Rate of heat generation
- Heat capacity measurement
- Quantity of evolved gas
- Rate of gas evolution
- Accumulation
- Define process envelope
- Cooling requirement
- Ease of initiation
RC1 Reaction Calorimeter

Adiabatic temperature rise due to a reaction is defined as:

\[ \Delta T_{\text{adiabatic}} = - \frac{\Delta H}{C_p} \]

where
- \( \Delta H \) – heat of reaction
- \( C_p \) – average heat capacity of the reacting mixture
- \( \Delta T_{\text{adiabatic}} \) – adiabatic temperature rise
Alternatives to the ARC

\[ \phi = \frac{m_s C_{V_s} + m C_V}{m C_V} \]

- Phi factor (≥ 1 for a typical industrial vessel)

\( C_V \) - Heat capacity of the reacting mixture (cal/mol K)

\( C_{V_s} \) - Heat capacity of the sample cell (cal/mol K)
What does the ARC look like?
Accelerating Rate calorimeter (ARC)
Accelerating Rate calorimeter (ARC)

Used to evaluate starting materials, intermediates, reaction mixtures and products under near-adiabatic conditions

Typical mode of operation:
Heat – Wait – Search (HWS)

\[
\phi = \frac{m_z C_{Vs} + m C_V}{m C_V} \quad \text{- Phi factor (≥ 1 for a typical industrial vessel)}
\]

- \( C_V \) - Heat capacity of the reacting mixture (cal/mol K)
- \( C_{Vs} \) - Heat capacity of the sample cell (cal/mol K)
ARC Data for HOBT Decomposition

Temperature (°C) vs. Time (minutes)

- Temperature: 100°C to 260°C
- Time: 600 to 1260 minutes

Pressure (bar) vs. Time (minutes)

- Pressure: 0 bar to 160 bar
- Time: 600 to 1260 minutes

Legend:
- Red line: Temp (°C)
- Green line: Pres (bar)
Sample size: 2.1732 g  
Bomb type: HC-LCQ  
phi factor: 2.2959

Onset of 1st exotherm: 104 °C
Adiabatic temp rise (uncorrected): 26 K  
Estimated adiabatic temp rise (corrected): 66 K

Onset of 2nd exotherm: 164.5°C  
Adiabatic temp rise (uncorrected): 147.5 K  
Estimated adiabatic temp rise (corrected): 339 K
Nitro Compound (larger sample)
Flashpoint and Conductivity Measurements
Flash Point – What is it?

- Flash point is the lowest temperature at which the vapour of a combustible liquid can be made to ignite momentarily in air.

- Liquids are classified as either flammable or combustible based on their flash points - flammable liquids have flash point < 100 °F/38 °C.

- If an operation can be guaranteed to be undertaken 15 °C or more below the materials flash point, the process can be considered low risk (assumes sensible precautions taken, such as grounding of equipment and an absence of ignition sources).
## Classifications of Flammable Materials (NFPA)

<table>
<thead>
<tr>
<th>Classification</th>
<th>Term</th>
<th>Flash point and boiling point</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class IA</td>
<td>Highly Flammable</td>
<td>Fp below 21 °C, bp below 38 °C</td>
<td>diethyl ether, acetaldehyde, methyl formate, pentane</td>
</tr>
<tr>
<td>Class IB</td>
<td>Flammable</td>
<td>Fp below 21 °C, bp above 38 °C</td>
<td>acetone, benzene, carbon disulfide, ethanol, toluene, heptane, hexane</td>
</tr>
<tr>
<td>Class IC</td>
<td>Flammable</td>
<td>Fp above 21 °C, but below 38 °C</td>
<td>butanol, amyl acetate</td>
</tr>
<tr>
<td>Class II</td>
<td>Combustible</td>
<td>At or above 38 °C and below 60 °C</td>
<td>glacial acetic acid, formaldehyde, hydrazine</td>
</tr>
<tr>
<td>Class IIIA</td>
<td>Combustible</td>
<td>At or above 60 °C and below 93 °C</td>
<td>naphthalene, octyl alcohol</td>
</tr>
<tr>
<td>Class IIIB</td>
<td>Combustible</td>
<td>At or above 93 °C</td>
<td>glycerine, propylene glycol</td>
</tr>
</tbody>
</table>
Flammable Atmospheres

• The flammability of a vapour/air mixture is dependent on concentration and is defined by the flammable or explosive limits

• Lower Explosive Limits (LEL) / Lower Flammable Limits (LFL)
  - lowest concentration of vapour in air that will sustain a flame, burn or explode

• Upper Explosive Limits (UEL) / Upper Flammable Limits (UFL)
  - Highest concentration of vapour in air that will sustain a flame, burn or explode

• Auto ignition temperature is the temperature at which a material self-ignites without any obvious source of ignition
Detailed Review of Powders
Minimum Ignition Energy (MIE) Apparatus

Minimum Ignition Energy Apparatus MIEII

MIE of Gases/Vapors (Vapor test vessel and electrode assembly shown.)
Electrostatic Hazards

- Potential source of ignition energy is an accumulated electrostatic discharge. Some materials pose more serious risk than others. For example, hydrocarbons, symmetrical molecules such as ethers, and molecules with long carbon chains, like a C$_7$ or higher alcohol, all present a severe risk of electrostatic ignition.

- Two-phase systems such as wet toluene or solids suspended in low conductivity liquids can also increase the risk of ignition.
## Liquid Conductivity

- **Low Conductivity Liquid**: Electrical conductivity is less than 100 pS/m
- **Medium Conductivity Liquid (Semi-conductive)**: Electrical conductivity is between 100 and 10,000 pS/m
- **High Conductivity Liquid**: Electrical conductivity greater than 10,000 pS/m

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Conductivity (pS/m)</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>$6 \times 10^6$</td>
<td>Conductive</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>$7 \times 10^8$</td>
<td>Conductive</td>
</tr>
<tr>
<td>Isopropyl ether</td>
<td>500</td>
<td>Semi-conductive</td>
</tr>
<tr>
<td>Heptane</td>
<td>$3 \times 10^{-2}$</td>
<td>Non-conductive</td>
</tr>
<tr>
<td>Methanol</td>
<td>$1 \times 10^5$</td>
<td>Conductive</td>
</tr>
<tr>
<td>Toluene</td>
<td>&lt; 1</td>
<td>Non-conductive</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.1</td>
<td>Non-conductive</td>
</tr>
</tbody>
</table>
Electrostatic Hazard - Transfers

Control of Flow Velocity

- Liquids with conductivity > 100 pS/m, no flow velocity restrictions (no or little electrostatic charge generation)
- Liquids with conductivity ≤ 100 pS/m and no immiscible components, flow velocity should be less than 7 m/s
- Liquids with conductivity ≤ 100 pS/m and containing immiscible components, flow velocity should be less than 1 m/s

Personnel

- During normal activity, the potential of the human body can reach 10 kV to 15 kV, and the energy of a possible spark can reach 20 mJ to 30 mJ
Damage to Reactor Glass
Process Safety Methodology - Desktop Review

• Materials with high-energy bond groupings?
• Peroxidizable substances?
• Pyrophoric substances?
• Water reactive substances?
• Class 1 solvents (e.g. benzene, carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethylene, 1,1,1-trichloroethane)?
• Flammable gases, including by-products?
• Flammable liquids (flashpoint < 38 °C/100 °F)?
• Flammable solids?
• Combustible liquids (flashpoint ≥ 38 °C/100 °F)?
Process Safety Methodology - Desktop Review (2)

• Non-conductive solvents (conductivity < 100 pS/m)?
• Potential hazardous polymerizations?
• Spontaneously incompatible mixtures?
• Gases (include possible side-reactions and destructions)?
• Are any of the reagents used not on the DSL?
• Are there any Class A or Class B precursors used (Controlled Chemicals)?
• Are there any chemicals subject to the Chemical Weapons Convention?
• Reagents, intermediates or product with potential for hazardous decomposition?
• Reaction mixtures without a solvent present?
• Heterogeneous mixtures that are then heated to initiate the reaction?
### Highly-energetic Functional Groups

**Table 1. Highly Energetic Functional Groups**

<table>
<thead>
<tr>
<th>name/structure(^a)</th>
<th>range of decomposition energies(^b) (kJ·mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkenes (R₂C=CR₂)</td>
<td>50 → 90</td>
</tr>
<tr>
<td>alkynes/acetylenes (R–C≡C–R)</td>
<td>120 → 170</td>
</tr>
<tr>
<td>epoxides</td>
<td>70 → 100</td>
</tr>
<tr>
<td>peracids (R–CO–O–O–H)</td>
<td>240 → 290</td>
</tr>
<tr>
<td>organic sulfoxides (R₂S=O)</td>
<td>40 → 70</td>
</tr>
<tr>
<td>organic sulfonyl chlorides (R–SO₂Cl)</td>
<td>50 → 70</td>
</tr>
<tr>
<td>hydrazines (R–NH–NH–R)</td>
<td>70 → 90</td>
</tr>
<tr>
<td>diazo/diazonium (R–N=N=R/R–N=N=NO)</td>
<td>100 → 180</td>
</tr>
<tr>
<td>azides (R–N₃)</td>
<td>200 → 240</td>
</tr>
<tr>
<td>oxime (R₂C=NOH)</td>
<td>110 → 140</td>
</tr>
<tr>
<td>N-oxides (R₂N=O)</td>
<td>100 → 130</td>
</tr>
<tr>
<td>nitroso (R₂C–N=O)</td>
<td>150 → 290</td>
</tr>
<tr>
<td>isocyanate (R–N=C=O)</td>
<td>50 → 75</td>
</tr>
<tr>
<td>nitro (R₂C–NO₂)</td>
<td>310 → 360</td>
</tr>
<tr>
<td>N-nitro (R₂N–NO₂)</td>
<td>400 → 430</td>
</tr>
<tr>
<td>acyl nitrates (–O–NO₂)</td>
<td>400 → 480</td>
</tr>
</tbody>
</table>

\(^a\) R, in most cases, represents an organic fragment. \(^b\) Not exhaustive.

If a molecule \(\text{C}_2\text{H}_4\text{O}_2\) reacts completely with oxygen according to the stoichiometric equation:

\[ \text{C}_2\text{H}_4\text{O}_2 + (2x + y/2 - z)\text{O} \rightarrow x\text{CO}_2 + y/2\text{H}_2 \]

the oxygen balance is:

\[ -1600(2x + y/2 - z) = \text{molecular weight} \]
Peroxidizable Chemicals

- Chemicals that can form peroxides in storage, generally when in contact with air
- Peroxides that form are less volatile than the solvent itself and, thus, tend to concentrate
- If peroxides are present during a distillation, the applied heat to the concentrated solution may trigger a violent explosion
- Containers allowed to evaporate to dryness leaving crystals behind are extremely dangerous!
Peroxidizable Chemicals

- **List A**: Chemicals that may form explosive levels of peroxides without concentration by evaporation or distillation.
  - These materials are particularly dangerous because they can be hazardous even if never opened.

- **List B**: Chemicals that may form explosive levels of peroxides upon concentration.
  - Therefore, they have the potential of becoming far more hazardous after they are opened.

- **List C**: Chemicals that may autopolymerize as a result of peroxides accumulation.
  - These materials are typically stored with polymerization inhibitors to prevent these dangerous reactions.
Peroxidizable Chemicals

List A:
- Butadiene
- Potassium
- Chloroprene
- Divinylacetylene
- Potassium amide
- Sodium amide (sodamide)
- Isopropyl ether (diisopropyl ether, DIPE)
- Tetrafluoroethylene
- Vinylidene chloride (1,1-dichloroethylene)
Examples of List B Compounds

Acetaldehyde
Benzyl alcohol
Cumene (isopropylbenzene)
Cyclohexanol
2-Cyclohexen-1-ol
Cyclohexene
Decahydronaphthalene
Dicyclopentadiene
Diethyl ether
Diglyme (2-methoxyethyl ether)
Dioxanes
Glyme (1,2-dimethoxyethane)
4-Heptanol
2-Hexanol

Methylacetylene
Methylcyclopentane
Methyl isobutyl ketone
4-Methyl-2-pentanol
2-Methyltetrahydrofuran
2-Pentanol
4-Penten-1-ol
1-Phenylethanol
2-Phenylethanol
2-Propanol (isopropanol)
Tetrahydrofuran
Tetrahydronaphthalene
Vinyl ethers
Other secondary alcohols
Precautions for Handling Peroxide Forming Materials

- Never return unused quantities back to the container
- Avoid improper storage conditions: Do not freeze as this can cause the peroxide to precipitate out, and higher temperatures can speed up peroxide formation
- Avoid evaporation or distillation
- Use peroxide test strips to test for the presence of peroxides
- All sources of friction and grinding should be avoided
- Dilution of the organic peroxide with the appropriate inert solvent (aliphatic hydrocarbons) helps to reduce the sensitivity of the peroxide to shock and heat
- Segregate these compounds from others that could create a serious hazard to life or property should an accident occur
Inhibitors

• A chemical that is added to a material to slow down or prevent an unwanted reaction (e.g., peroxide formation and/or polymerization)

• Inhibitor levels in materials may gradually decrease during storage even at recommended temperatures

• An increase in temperature can decrease inhibitor levels
Oxidizers

- Compounds that readily give off oxygen or other oxidizing substances
- Oxidation reactions are usually very exothermic
- Can cause other materials to combust more readily or make fires burn more fiercely
- Oxidation reactions can be spontaneous at room temperature or with slight heating
- Oxidizers should be stored away from flammable and combustible materials
Pyrophoric compounds

- Reagents that are reactive towards oxygen (air), rapid oxidization
- Chemicals that ignite “on their own” below 55 °C.
  - Ignition can be essentially instantaneous, the time delay being measured in milliseconds
  - Ignition may be delayed
  - May only occur if the material is finely divided or spread out in a thin layer
Pyrophoric materials

- Grignard reagents, e.g., R-Mg-X
- Metal alkyls and aryls, e.g., RLi, RNa, R₃Al, R₂Zn
- Metal carbonyls, e.g., Ni(CO)₄, Fe(CO)₅, Co₂(CO)₈
- Alkali metals, e.g., Na, K
- Metal powders, e.g., Al, Co, Fe, Mg, Mn, Pd, Pt, Ti, Sn, Zn, Zr
- Metal hydrides, e.g., NaH, LiAlH₄
- Non-metal hydrides, e.g., B₂H₆ and other boranes, PH₃
- Non-metal alkyls, e.g., R₃B, R₃P
- Phosphorus (white)
- Used hydrogenation catalysts (especially hazardous because of the adsorbed hydrogen)
Water Reactive Compounds (1)

- Materials that react violently or explosively with water
- Pyrophoric materials are often water reactive as well and will ignite when they contact water or humid air
- Hazards involved when material is exposed to water
  - release of flammable gas
  - release of strong oxidizing gas
  - release of toxic gas
  - release of metal oxide fumes
  - formation of corrosive acids
Water Reactive Compounds (2)

- Alkali metals, e.g., Na, K
- Alkali metal hydrides, e.g., NaH
- Alkali metal amides, e.g., NaNH₂
- Metal alkyls, e.g., lithium alkyls and aluminum alkyls
- Grignard reagent, e.g., R-Mg-X
- Halides of non-metals, e.g., PCl₃, PCl₅, PBr₃
- Anhydrous metal halides, e.g., AlCl₃, SnCl₄
- Inorganic acid halides, e.g., POCl₃, SOCl₂, SO₂Cl₂
- Calcium carbide
- Organic acid halides and anhydrides, of low molecular weight
Precautions for Pyrophoric and Water Reactive Materials

- Pyrophoric materials should be stored in tightly closed containers under an inert atmosphere (or inert liquid)
- Transfers should be carried out under an inert atmosphere
- Water reactive chemicals should never be stored under the sink or near water sources
- They can be handled safely in atmospheres of nitrogen or argon
- Most pyrophoric fires should be extinguished with a class D fire extinguisher
Process Safety Methodology (MASS)

CHART 2

SEMI BATCH OPERATION - ADDITION CONTROLLED REACTIONS

- **EXCIT L 1.1**
  - ΔH OF REACTION
  - L 2.1:
    - < 50 cal/g
  - L 2.2:
    - 50-200 cal/g
    - PRIMARY PROTECTION
    - Explosibility testing CHART 4
  - L 2.3:
    - > 200 cal/g
  - M 1.1:
    - 50-150 cal/g
    - DSC on product ΔHp
  - M 2.1:
    - < 50 cal/g
  - M 2.2:
    - 50-200 cal/g
    - explosive
    - Explosibility testing CHART 4
  - M 2.3:
    - > 200 cal/g
    - explosive
    - To be referred to G.S.H.
  - M 3.1:
    - (Ton SD - Top) > 50°C
    - (Ton DSC - Top) > 50°C
    - PRODUCT ONSET Ton SD or Ton SD
    - To be referred to G.S.H.
  - M 3.2:
    - (Ton DSC - Top) = 50 to 100°C
    - As per exit M 3.1 plus emergency douse

- **EXIT L 1.1**
  - ΔH OF REACTION
  - H 1.1:
    - > 150 cal/g
    - DSC on product ΔHp
  - H 2.2:
    - To be referred to G.S.H.
  - H 2.1:
    - ≤ 200 cal/g
    - PRODUCT ONSET Ton DSC

**Notes**:
1. If there is adequate control for avoiding accumulation
2. For setting conditions of activation of safety devices
3. Dewar onset for systems with a ΔHp > 200 cal/g

**Primary Protection and**
1. Addition to stop on agitator failure/coolant failure/reaction not proceeding i.e. too lower temperature
2. Check for accumulation
3. Independent temp/alarm
Process Safety Methodology - Overview

MTSR – maximum temperature of the synthesis reaction

TMR_{ad} – time to maximum rate under adiabatic conditions
$$T_{MR_{ad}} = \frac{c_p' \cdot R \cdot T_0^2}{q_0' \cdot E}$$
TMR\textsubscript{ad} – Estimation Methods (2)

ARC Data for HOBT Decomposition

Sample size: 0.544 g
Bomb type: HC-LCQ
\( \phi \) factor: 9.76

Onset of exotherm: 155 °C
Adiabatic temp rise (uncorrected): 78 K
Estimated adiabatic temp rise (corrected): 759 K
Stoessel Criticality Index

<table>
<thead>
<tr>
<th>Criticality Class</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td>MTSR</td>
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</tbody>
</table>

- **T<sub>p</sub>** – process temperature
- **T<sub>D24</sub>** – temperature at which TMRad is 24 hours
- **MTSR** – maximum temperature of the synthesis reaction
- **MTT** – maximum temperature for technical reasons

Criticality classes range from the least critical (1-2) to the most critical (3-5)
Flixborough (Nypro UK) Explosion, 1st June, 1974
Flixborough (Nypro UK) Explosion, 1st June, 1974
Flixborough (Nypro UK) Explosion, 1st June, 1974

• At about 16:53 hours on Saturday 1 June 1974 the Nypro (UK) site at Flixborough was severely damaged by a large explosion. Twenty-eight workers were killed and a further 36 suffered injuries. Offsite consequences resulted in fifty-three reported injuries. Property in the surrounding area was damaged to a varying degree.

• Prior to the explosion, on 27 March 1974, it was discovered that a vertical crack in reactor No.5 was leaking cyclohexane. The plant was subsequently shutdown for an investigation. The investigation that followed identified a serious problem with the reactor and the decision was taken to remove it and install a bypass assembly to connect reactors No.4 and No.6 so that the plant could continue production.

• Eighteen fatalities occurred in the control room as a result of the windows shattering and the collapse of the roof. No one escaped from the control room. The fires burned for several days and after ten days those that still raged were hampering the rescue work.
Case Study 1: Oxidation using Hydrogen Peroxide

R\textsuperscript{+} + H\textsubscript{2}O\textsubscript{2} \xrightarrow{\Delta} ACOH R=NH\textsuperscript{+} + H\textsubscript{2}O

- Oxidation reaction – expected to be energetic
- Order of charging
- Trapping solution in valves, or between valves
- Toxic nature of hydrogen peroxide
- Safe operating temperature of 100 °C
- Oxygen gas evolution
- Flash point of system (acetic acid - Fp 40 °C)
- Consideration of next processing step
Case Study 2: Nitration Reaction

- Nitration reaction – energetic starting material and product, and lower onset temperature for reaction mixture
- Previous reaction mixture – acetic acid
- Heat of mixing nitric acid and sulfuric acid
- Generation of NO\textsubscript{x} gases – flammability issues
- Reaction accumulation
- Compatibility (e.g., iron)
- Safe parameters for drying the product (rise time, 200-400 psi: 1.42 seconds for starting material, 0.02 seconds for product)
DSC Data for Nitration Product

Method: Standard 25-350/5/Glass
25.0-350.0°C 5.00°C/min  N2, 50.0 ml/min

Integral  5126.76 mJ
normalized  2500.86 Jg^-1
Onset  213.93 °C
Peak  231.55 °C

Integral  -238.42 mJ
normalized  -116.30 Jg^-1
Onset  92.21 °C
Peak  93.48 °C

Note: No weight loss recorded upon completion of test

Lab: Alberta

STAR® SW 10.00
Carius Tube Data for Nitration Product
Dosing of mixed acids (fuming nitric acid corrected to 92.5%)

Observed heat of reaction is -119.8 kJ per mole of starting material, equivalent to an adiabatic temperature rise of 98 °C. For the observed heat output, about 75% occurred during dosing; i.e., about 25% occurred after the dosing was complete.
RC1 Data Comparison

Comparison of Heat Outputs

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Heat output (W)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Qr (AJS-17)</td>
</tr>
<tr>
<td></td>
<td>Qr (AJS-20)</td>
</tr>
</tbody>
</table>

- Dosing
- $77^\circ C$
- $70^\circ C$
Hazards in Chemical Processing

The four main events that individually, or jointly, have the potential to cause significant harm or damage:

- Fire
- Explosion
- Release of Toxic Substances
- Release of Corrosive Substances

The four major hazards in chemical processing:

- Chemical reaction hazards (Reactivity)
- Fire and explosion hazards (Fire)
- Health hazards (Toxicity)
- Environmental hazards (Environment)