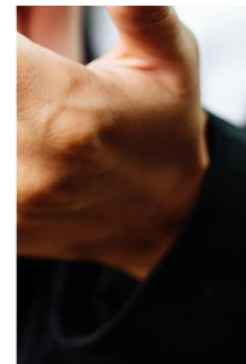


2021 Medals and Prizes

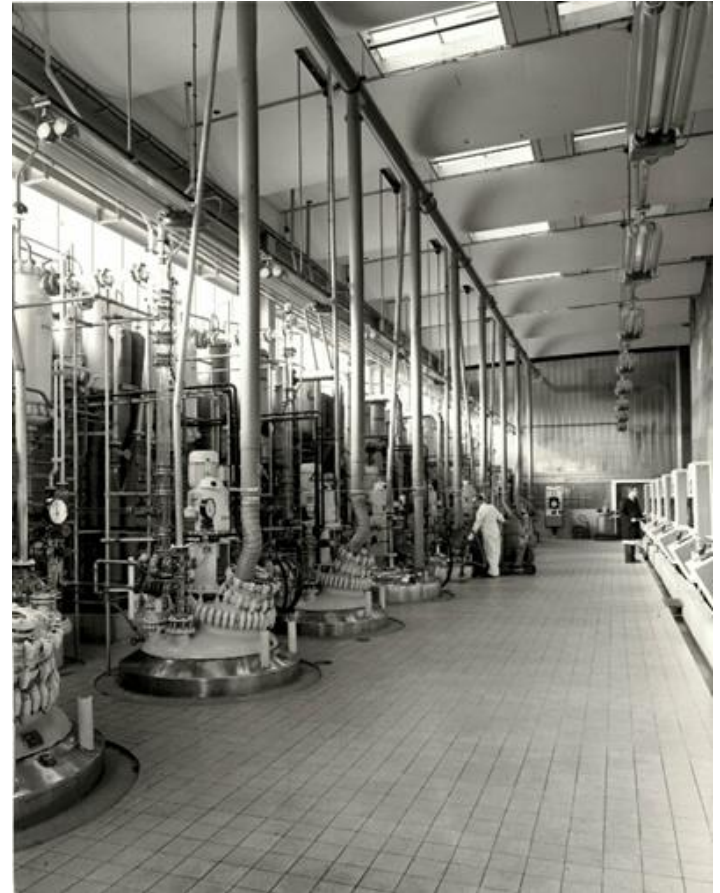
Lees Medal Winner – Mr Michael Rantell



Lees Medal Webinar

Background – A 1960's Pharmaceutical Intermediates Facility

- Opened in 1967
- 18 Reactors (plus centrifuges, paddle dryers, measure vessels etc)
- Multipurpose – reconfigure to make multiple products
- Still operating in 21st century, until demolished 2009



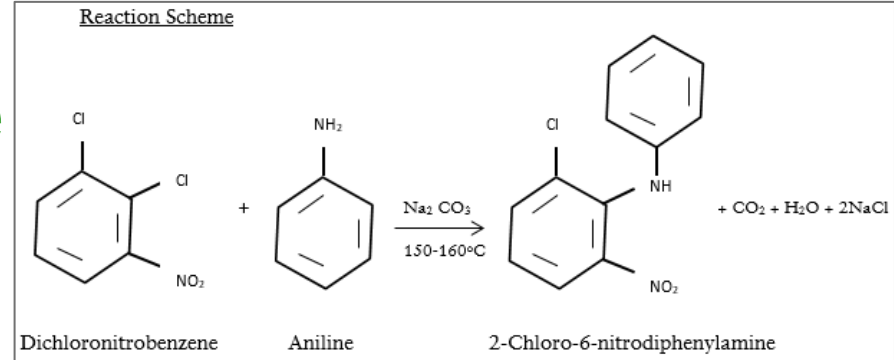
Reactor Floor 1967



Dial Pen Recorder



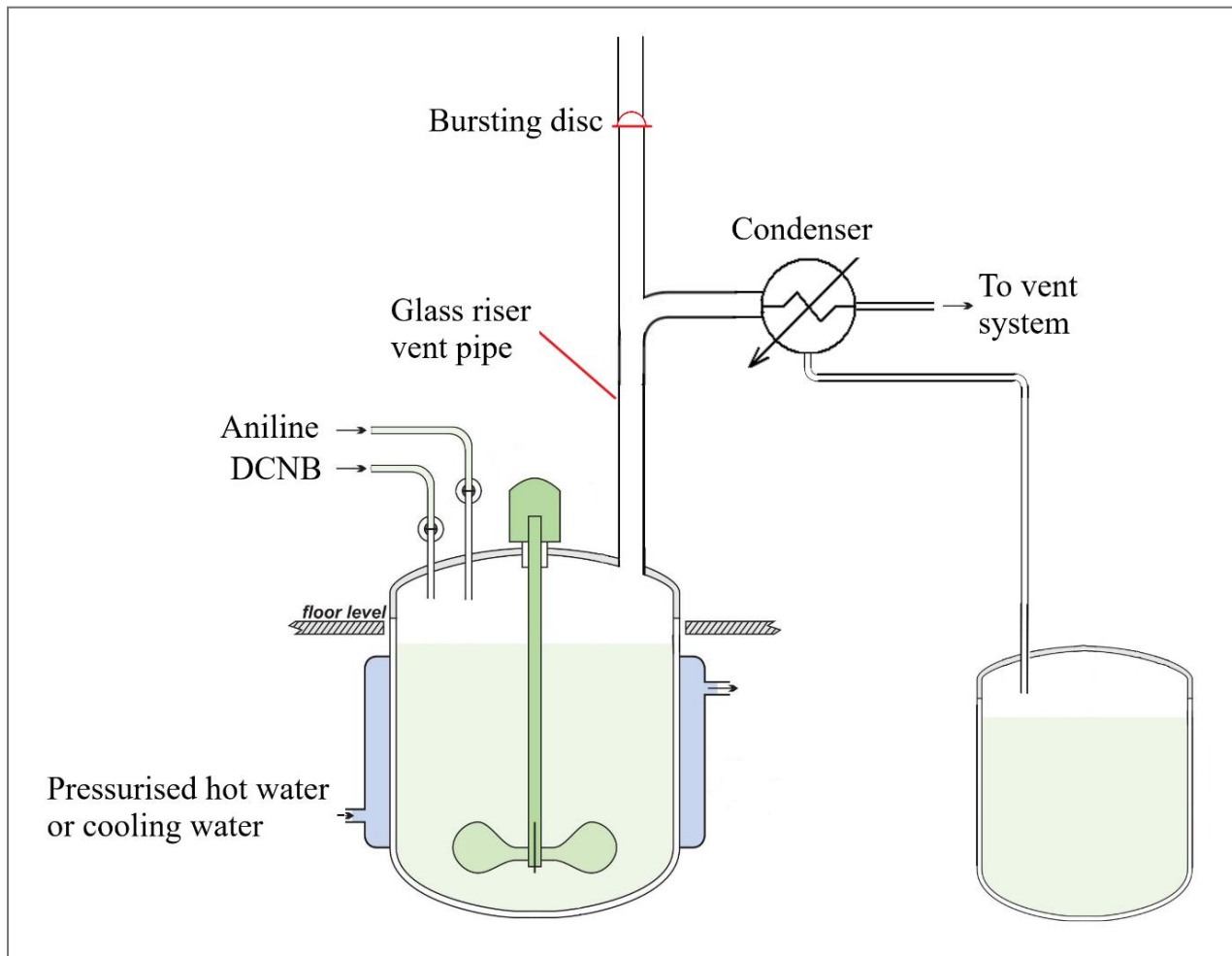
The Reaction Scheme



- Entire reaction occurs at atmospheric pressure and under nitrogen blanket
- Charge Sodium Carbonate Powder to reactor
- Charge Aniline from bulk storage to reactor
- Charge Molten DCNB (70 to 80c) from bulk storage to reactor
- Heat to ca 160c and hold for completion of reaction
- Sample and test for completion of reaction



Plant Set-up



- Glass lined Mild Steel Reactor, design pressure 6barg
- Glass “Riser” vent pipe and glass condenser
- Bursting Disc Pressure relatively low due to pressure rating of glass vent systems (ca 1.5barg)
- Jacket system was a pumped water circulation with live steam mixing – manual control



What Happened: 03-Jan-1992

Date/Time	Step
03Jan / 17:55	Charging of raw materials completed
03Jan / 21:15	Batch completed heating to 154c and steam/jacket turned off
03Jan / 22:00	Temperature = 158c, start of 16hr hold for reaction
03Jan / 23:30	Temperature = 169c (normally temperature then starts to fall)
04Jan / 02:00	Temperature >170c (instrument limit), aniline beginning to distill Technicians suspect passing steam valve and investigate
04Jan / 03:30	Temperature >170c, jacket now vented
04Jan / 05:00	Temperature >170c, aniline distilling vigorously
04Jan / 05:40	Reactor pressure = 0.5barg, cooling applied to jacket, agitator stopped
04Jan / 05:47	Reactor pressure = 1.5barg, fire alarm activated, building evacuated
04Jan / 05:49	Bursting discs blown, vigorous emission through roof vent which died down, then a second even more vigorous emission that died down after a further 5 to 10 minutes Batch released from glassware joints onto reactor floor

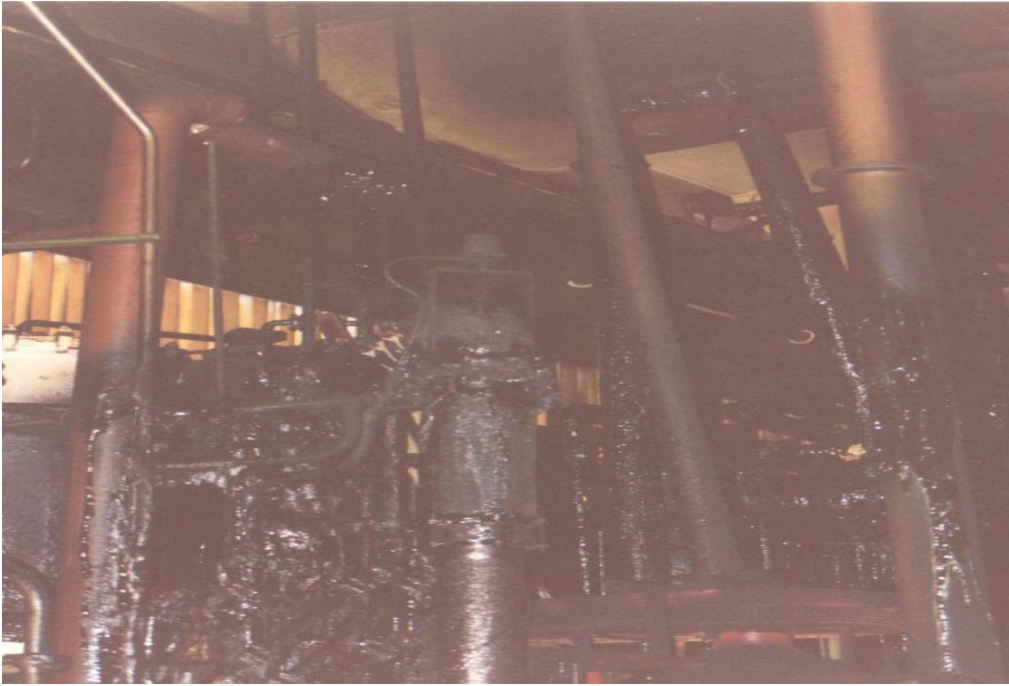


What it was like to be there

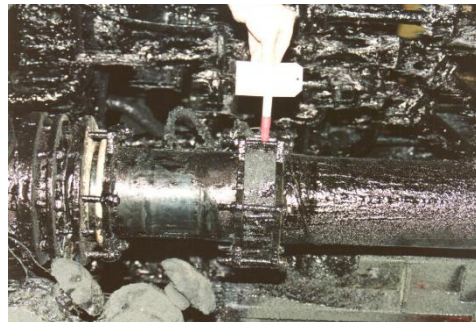
- Robert had only worked for the company for 6 months
- First opportunity to operate the process by himself after a period of shadowing more experienced technicians
- Handover showed no issues, expecting “a steady shift”
- Shift supervisor provided support / investigation when the process started to deviate
- They struggled to understand why this was happening
- Venting the jacket was “deafening”
- Evacuation was calm, it was only after seeing the roof emission and batch residues on the reactor floor, that the potential of the incident was realised



The Impact



- Back-pressure from thermal runaway had caused glassware joints to fail
- Decomposed batch released onto reactor floor
- No-one was hurt

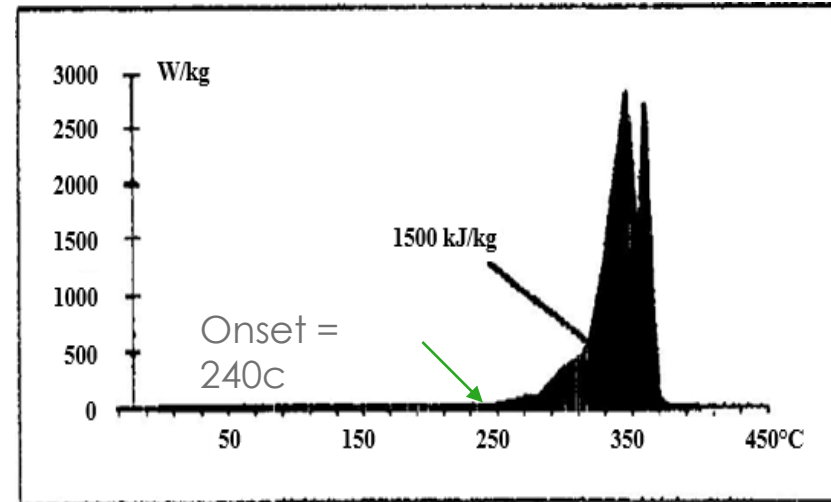


Slide 7

Reaction Thermal Data

- Differential Scanning Calorimetry measures the energy output from decomposition.
- 1500 kJ/kg equates to a theoretical temperature rise of 938c – high severity
- Exotherm onset temperature measured at 240c.
 - This is the temperature at which DSC first detects the exotherm and depends on the sensitivity of the machine
- Key point – decomposition is active below the DSC onset temperature of 240c
- At the normal operating temperature of 170c, the decomposition reaction was already active

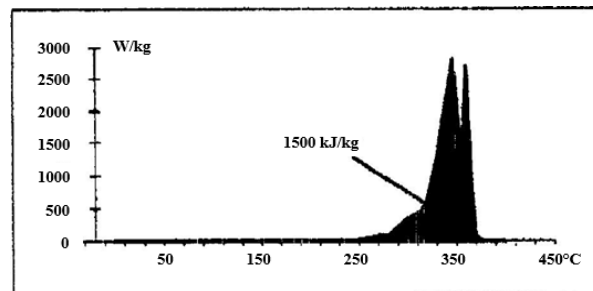
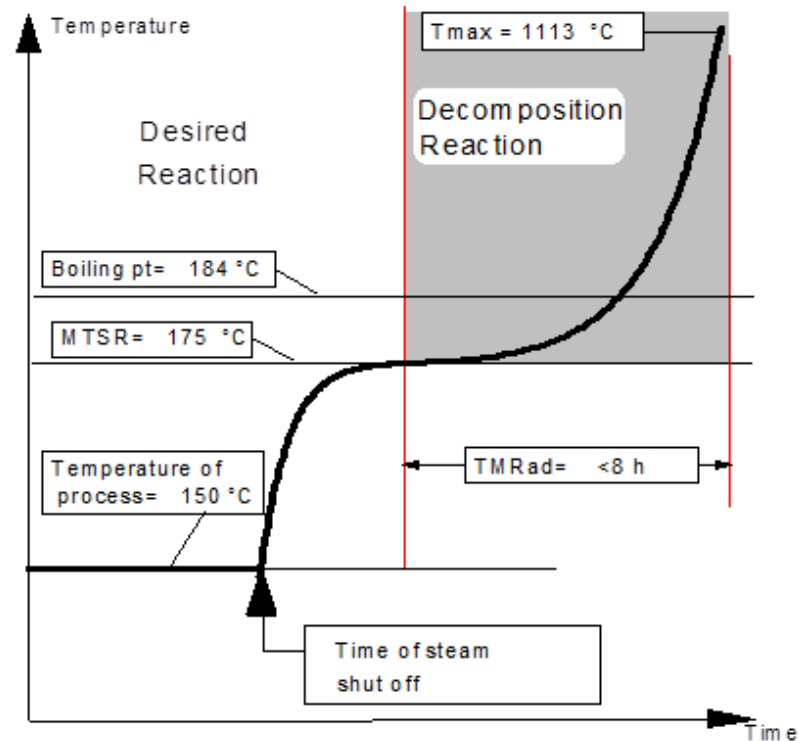
DSC data measuring the decomposition reaction



Reaction Thermal Data

- Synthesis reaction exotherm approx. 25c
- This takes T to 175c. Maximum Temperature of Synthesis Reaction (MTRSR)
- Time to maximum rate (TMRad) is how long until runaway under adiabatic conditions
- TMRad measured at <8hrs at 175c. High probability of runaway.
- Aniline boiling point = 184c, hence batch temperature stabilises here
- However, total energy of decomposition more than enough to boil off all the Aniline
 - Ineffective boiling barrier
 - The distillation return line was spaded – this could have prevented the runaway

SCENARIO



Shift Team Response

- During investigations jacket observed at 5 barg and rising – assumption made that there was a problem with the steam supply / passing valves
- No understanding initially that the reactor contents was heating the jacket, not vice versa
- Eventually an attempt was made to divert distillate back to reactor – however a spade made this impossible
- Just before evacuation, jacket was put onto cooling and agitator turned off
 - Cooling clearly the right decision, if done earlier would have prevented incident
 - Turning agitator off though reduces heat transfer, so better to leave agitator on
 - probably due to the inherent belief that the jacket was the cause



Immediate Causes

- Steam turned off at slightly higher temperature than normal (154c vs 150c) – slightly increased end of reaction temperature
- Minor overcharge of DCNB (3%) – also slightly increased end of reaction temperature
- Historical minor increase in batch size (10%)

Cumulative effect of these on a highly thermally sensitive process enough to tip the balance



Root Causes & Contributing Factors

- Basis of safety was Aniline as a boiling barrier – this was ineffective
- Process Design was not sufficient
 - Lack of distillate return to reactor meant that decomposition reaction removed the Aniline from the batch
 - If set to reflux instead, returning Aniline stabilises the temperature
 - No emergency cooling to ensure reflux and/or jacket cooling in the event of eg site power failure
 - Insufficient temperature control – turning jacket off at approx. 150c leads to variation from person to person. Steam turned off at 154c in incident
- Inadequate instrumentation
 - Process frequently operated outside range of temperature transmitter
 - Measured range clearly not suitable for credible deviations



Process Safety Management Gaps

CCPS Process Safety Management Element		Gap from incident
8	Process knowledge management	The management / technical staff understanding of the thermal hazards had been diluted with time
9	Hazard identification and Risk Analysis	The design of the process was not sufficient for the risk
10	Operating procedures	The method of temperature control was insufficient
15	Management of change	An accumulation of minor changes was enough to impact the safety of the process – creeping change
17	Conduct of operations	Routinely operating outside the measured range was accepted
18	Emergency management	No plans were in place how to react to a decomposition event



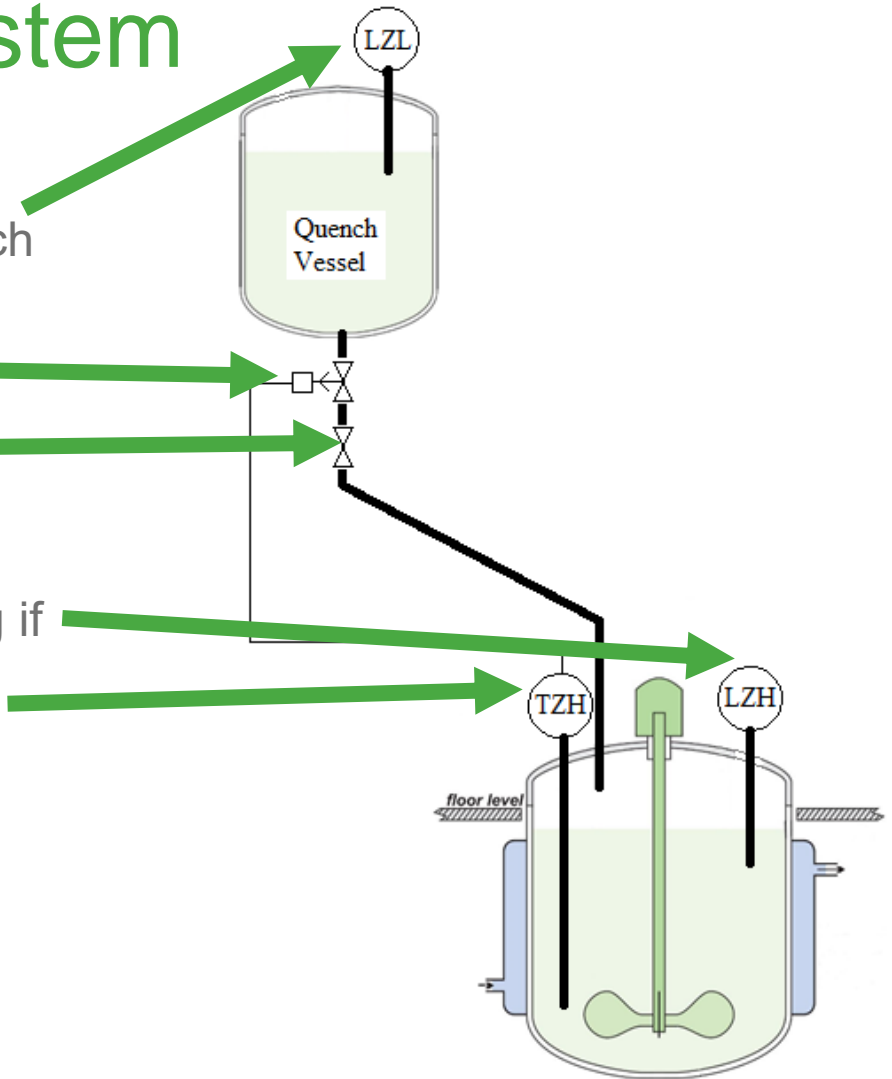
How to Redesign the process

Item	Approach
Inherent Safety	Is there a safer reaction scheme that avoids the decomposition hazard
Reduce the hazards	Is semi-batch possible: Adding the 2 nd reactant portion-wise throughout the reaction – reaction can be stopped
Control the temperature	Automatic temperature control would allow the jacket to respond to any minor deviation
Guarantee the boiling barrier	Set the reactor to reflux during reaction – the distilled solvent returns to the reactor and stabilises the temperature at the boiling point Must also ensure condensers can continue to operate
Emergency cooling	Ensures that condensers can still operate Ensures jacket can be cooled in an emergency
Quench system	Alternative approach is to cool & dilute the batch with an appropriate solvent when critical temperature is reached



Example Quench System

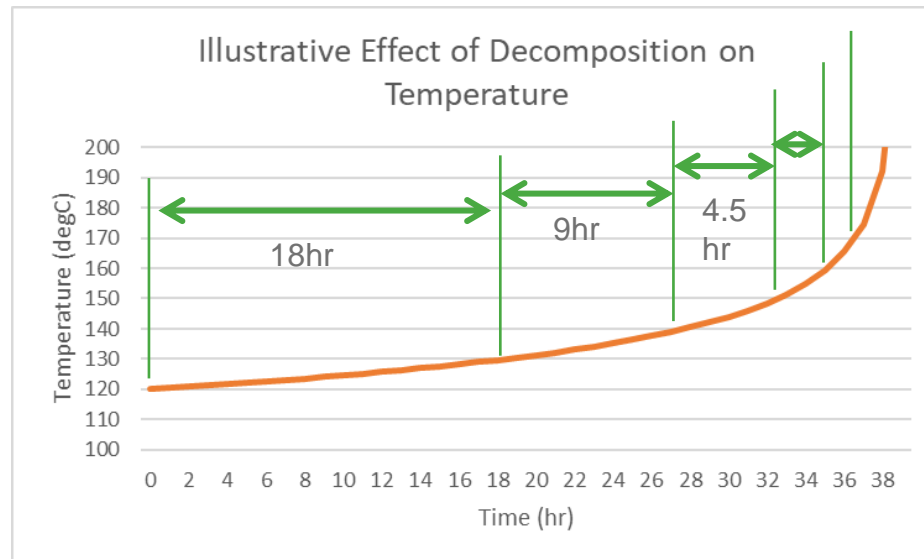
- LZL – don't allow batch to start if quench vessel is not full
- Auto-valve – fail open
- Manual valve – potential to override quench – Lock it open and define as a critical task
- LZH – don't allow batch to start heating if not enough room in vessel for quench
- TZH – high temperature trip to activate quench



Assessing Decomposition Hazards

- Decomposition reaction rate often follows Arrhenius equation
 - $k=Ae^{(-E/RT)}$
- Exponential increase in rate with temperature
- For illustrative purposes assume rule of thumb – rate doubles every 10degC, and slow decomposition is giving 0.4degC per hr rise at point of cooling failure
- Mathematically 0.4degC per hr rise has become infinite within 40hrs – thermal runaway

Time to increase by 10degC halves each period



Assessing Decomposition Hazards

Evaluate severity

- Is adiabatic temperature rise $>50^{\circ}\text{C}$ – medium severity
- Is adiabatic temperature rise $>200^{\circ}\text{C}$ – high severity

Evaluate MTSR

- MTSR - Maximum temperature batch can reach on loss of cooling

At MTSR

- Can decomposition be triggered at MTSR
- Is time to runaway $<24\text{hr}$ - critical
- Is time to runaway $<8\text{hr}$ – highly critical

At BP

- Does batch reach boiling point before triggering decomposition
- Yes – is boiling barrier sufficient to prevent decomposition - critical
- No – is boiling barrier sufficient to cope with decomposition – highly critical

Re-design?

- If boiling barrier is not sufficient, redesign the process
- Add emergency cooling and/or quench system
- Re-design to remove / reduce the hazards



Final Words

Root Cause: Insufficient basis of safety and specifically an inadequate boiling barrier

Contributory factors: Creeping change – batch size change, and minor over charge

Questions to ask yourself:

- Do you have full thermal safety data for your reactions and does it represent current good industry practice?
- What changes has your process undergone and so does the data reflect the process you operate today?
- What is the basis of safety for the reaction scheme?
- Is the basis of safety robust to foreseeable deviations and mal-operation?



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