Thermal Process Safety
Criticality Classes as a Tool for Assessment and Design

EPSC Award Lecture

Francis Stoessel

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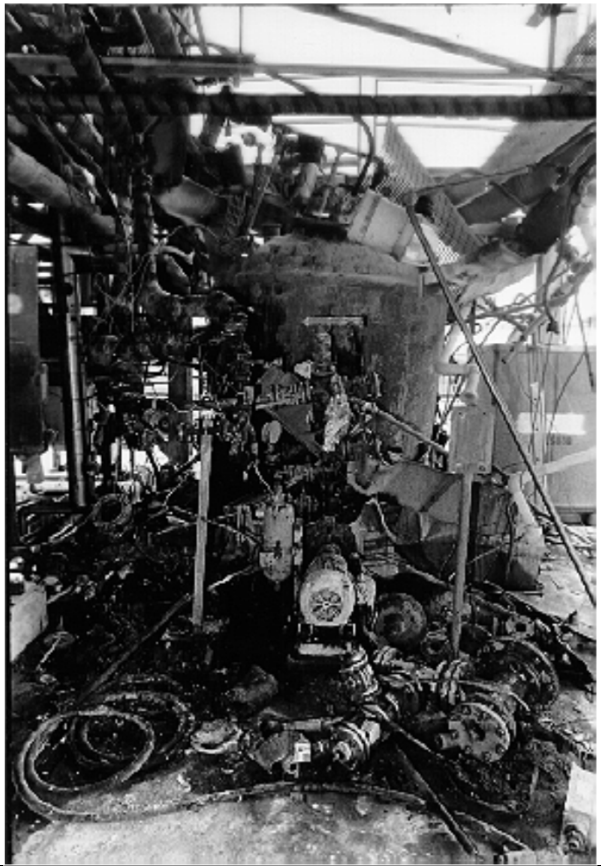
Thermal Process Safety
Criticality Classes as a Tool for Assessment and Design

- **Learning from Incidents**
- Simplification of Thermodynamics
- Systematic Risk Assessment Procedure
- From Risk Assessment to Protection Strategy
- From Risk Assessment to Design

Three Incidents in 1992 January, April, July



Thermal Process Safety Knowledge (Lessons Learned)

- Knowledge available in Safety Laboratories
  - Core competence

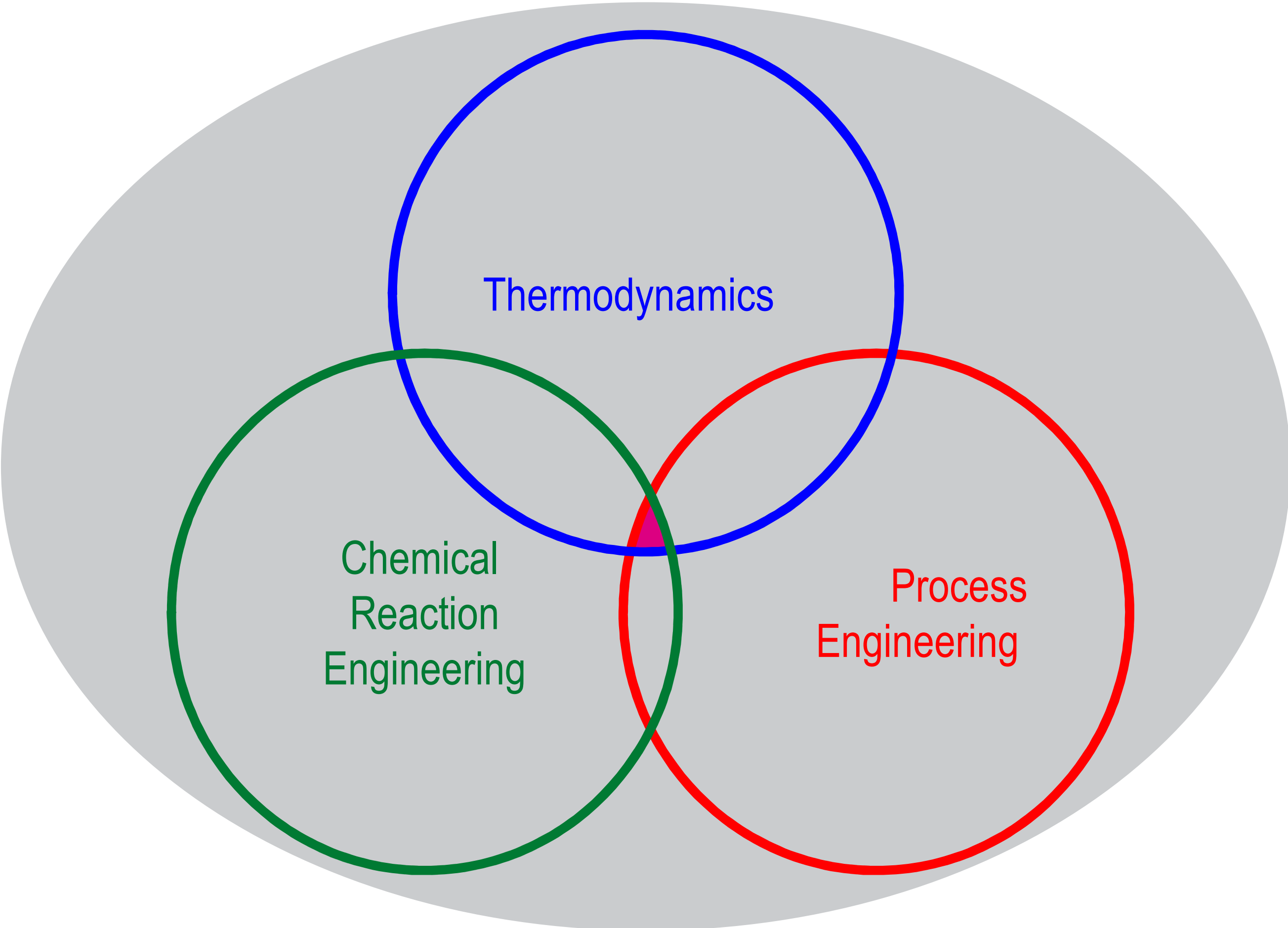
Must also be available in Operation

- Process developement
  - Focus on chemistry, yield
- Production plants
  - Focus on quality, delivery, plant management

Thermal Process Safety

At the intercept of three professions

- Thermodynamics
  - Physical chemistry
  - Kinetics
- Reaction Engineering
  - Chemical reaction engineering
  - Process technology
- Process Engineering
  - Automation and process control
  - Safety systems



Knowledge transmission

- Ensure Communication
  - Common and simple language
- Complex concepts must be made understandable
  - Requires simplification
  - Without loosing the scientific roots
- Training program
  - Production
  - Process development
- Tools
  - TST: Thermal Safety Tutorial
  - TSA: Thermal Safety Assessment

Thermal Process Safety
Criticality Classes as a Tool for Assessment and Design

- Learning from incidents
- **Simplification of thermodynamics**
- Systematic Assessment procedure
- From Risk Assessment to Protection Strategy
- From Risk Assessment to Design

Simplification is required

Typical sentence in a safety report before 1992

A decomposition reaction with a specific energy of 500 J/g
releases 10 W/kg at a temperature of 150 °C.

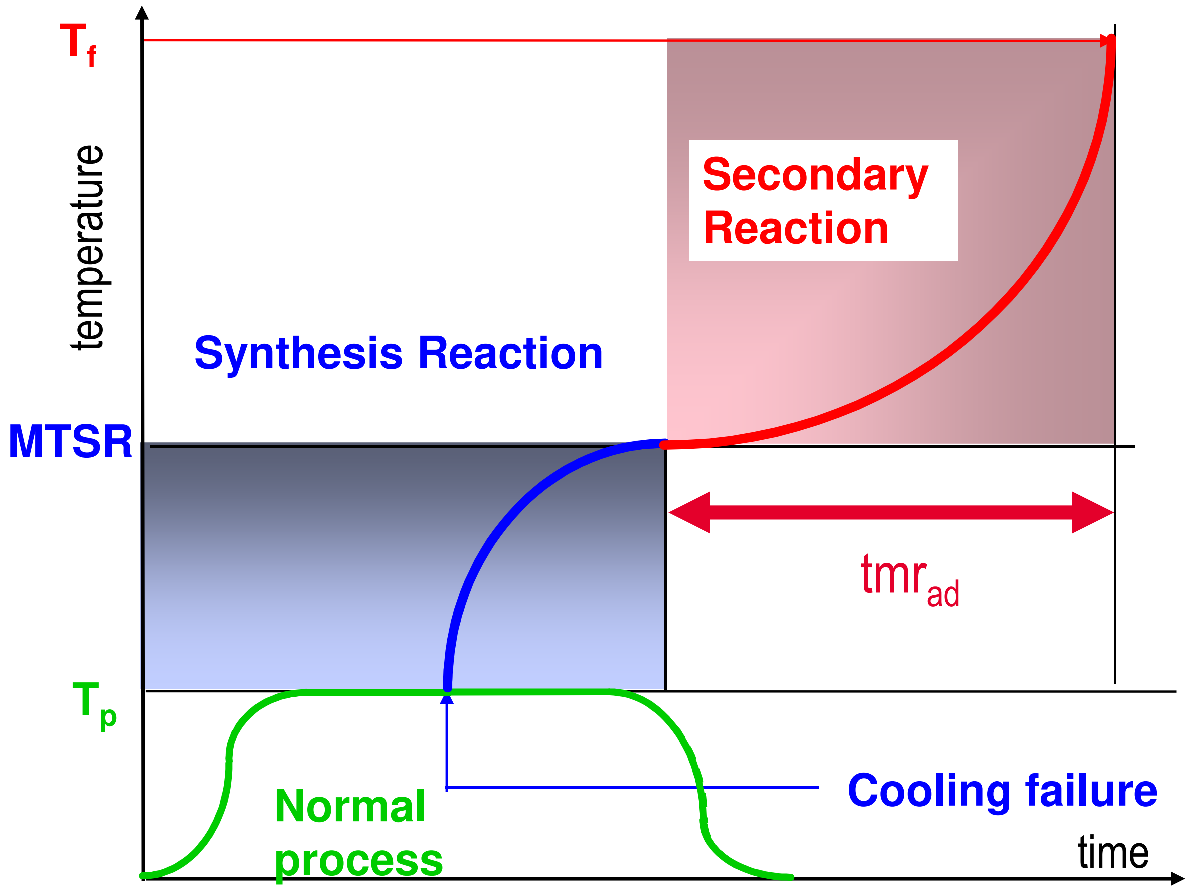
Assuming a process temperature of 150 °C: Is the process critical or not?

Cooling Failure Scenario

- Runaway profile T = f(T)

Thermal Safety Characteristics

- T_p Process temperature
- MTSR Maximum temperature of the synthesis reaction
- T_f Final temperaure
- tmr_{ad} time to maximum rate under adiabatic conditions



Risk Assessment Criteria

- Severity on temperature scale
  - The higher the temperature
    the higher the pressure
    the higher the damage
- Probability on time scale
  - The shorter the time available to recover a safe situation
    the higher the probability of runaway

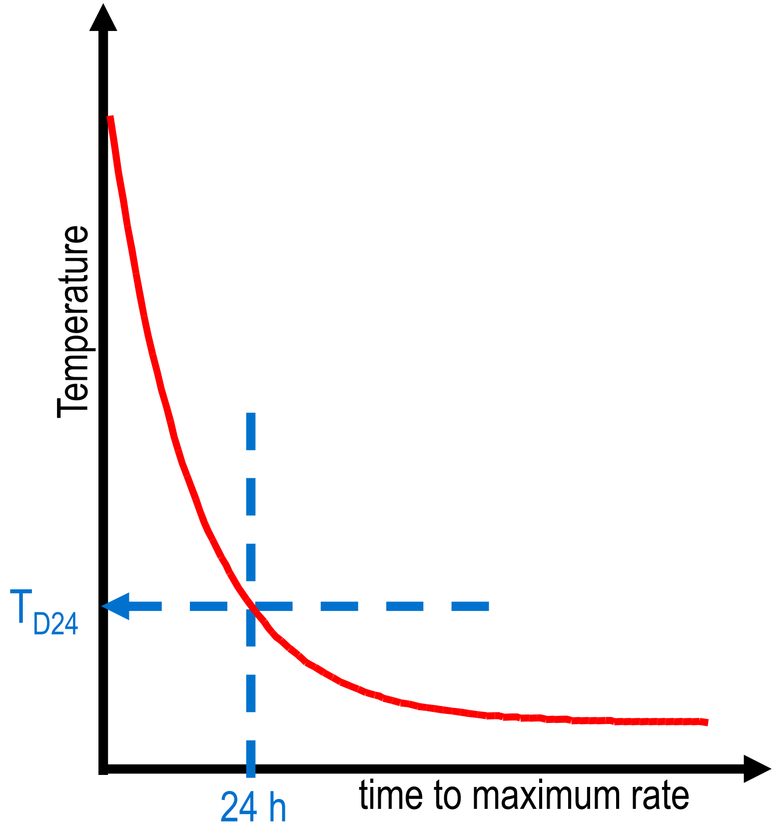
Severity	High	$\Delta T_{ad} > 200K$			
	Medium	$50K < \Delta T_{ad} < 200K$			
	Low	$\Delta T_{ad} < 50K$ and no pressure			
			$tmr_{ad} \geq 24h$	$8h < tmr_{ad} < 24$	$tmr_{ad} \leq 8h$
			Low	Medium	High
			Probability		

From tmr_{ad} to T_{D24}

- tmr_{ad} is a time
- It is an exponential function of temperature

$$tmr_{ad}(T_0) = \frac{c_p R T_0^2}{q_{ref} \exp\left[\frac{-E}{R}\left(\frac{1}{T_0} - \frac{1}{T_{ref}}\right)\right] E}$$

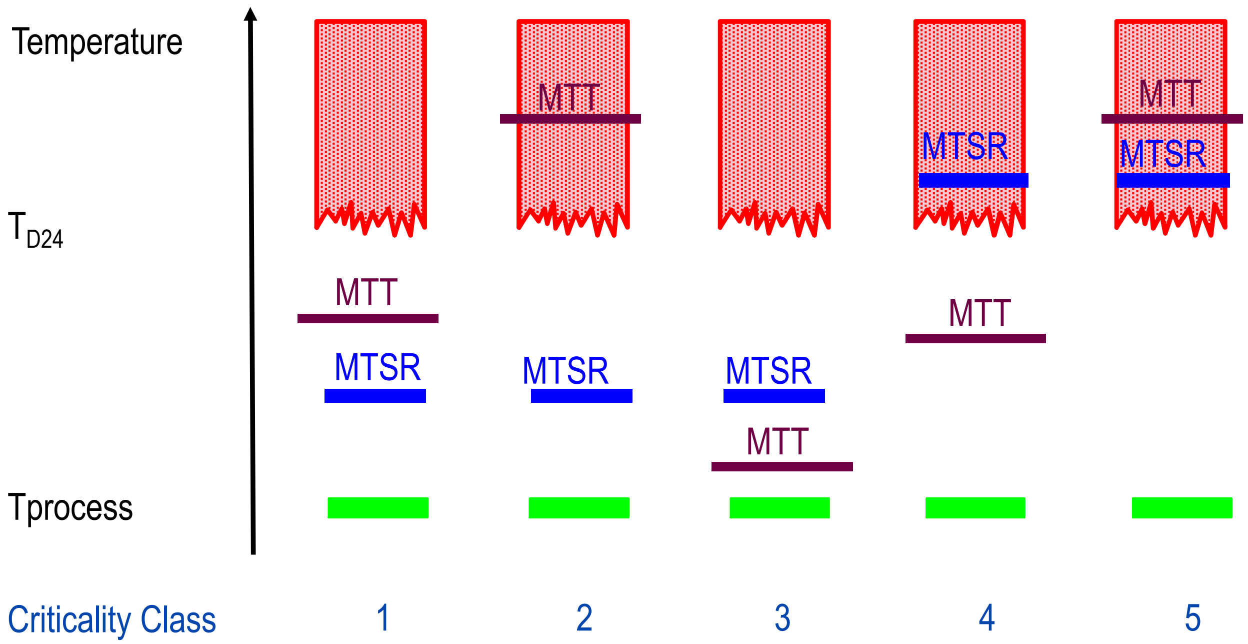
- T_{D24} The temperature at which the tmr_{ad} is 24 h.



Criticality Classes

- T_p Process temperature
- MTSR Maximum temperature of synthesis reaction
- T_{D24} Maximum temperature for thermal stability
- MTT Maximum temperature for technical reasons

○ T_f Final temperature

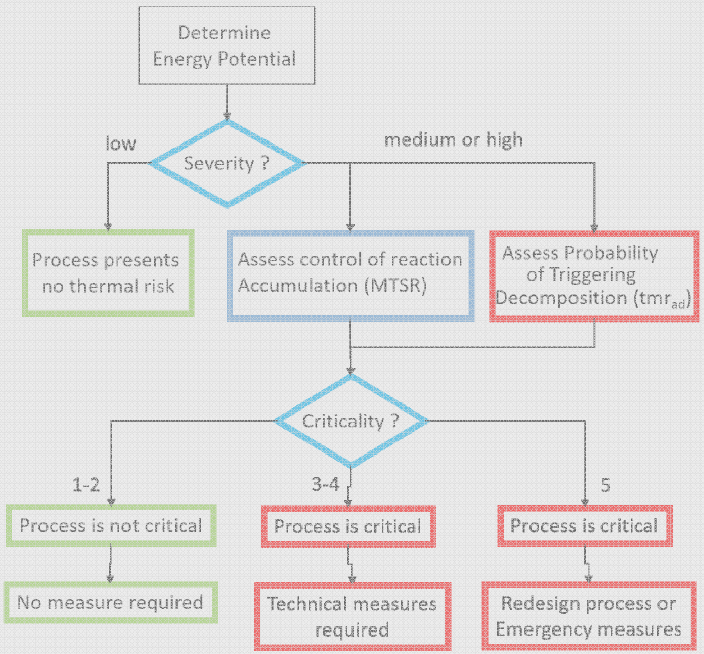


Simplification

Simple language built on scientific roots

- A decomposition reaction with a specific energy of 500 J/g releases 10 W/kg at a temperature of 150°C.

- A decomposition, able to raise the temperature by 250 °C, leads to a severe thermal explosion within less than one hour, starting from 150 °C.

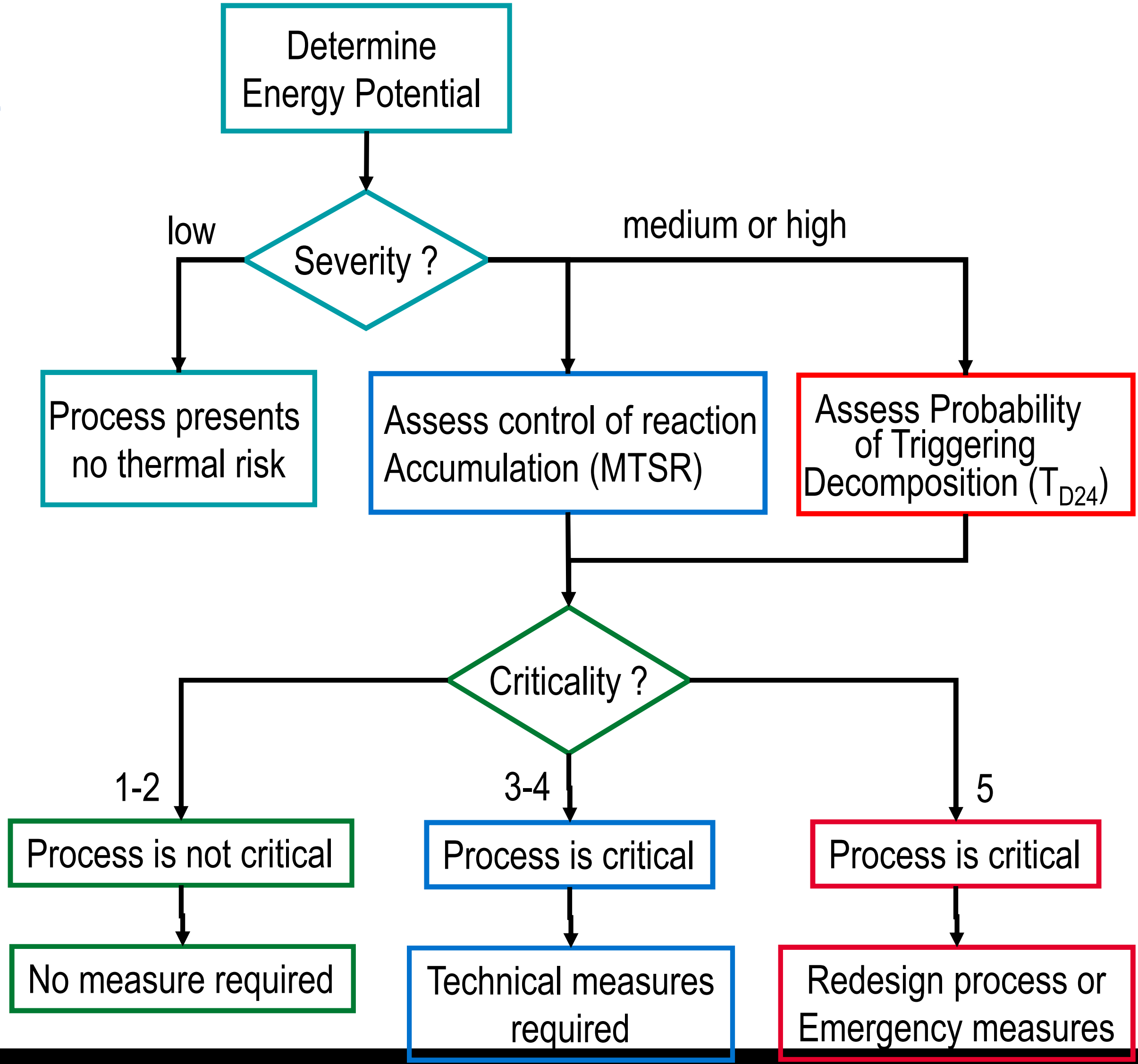


Thermal Process Safety
Criticality Classes as a Tool for Assessment and Design

- Learning from Incidents
- Simplification of Thermodynamics
- **Systematic Assessment Procedure**
- From Risk Assessment to Protection Strategy
- From Risk Assessment to Design

Assessment Procedure

1. Determine Energy potential
2. Determine the 4 characteristic temperatures
3. Criticality class
4. Assessment
5. Directions for design of measures



Example Condensation Reaction

Process Description

- Solvent: Acetone
- Charge: 2500 kg
- Reaction temperature: 40 °C.
- Semi-batch with stoichiometric addition within 2 hours
- Maximum accumulation is 30%.

Reaction:	$Q'_r = 230\ \mathrm{kg\,kg^{-1}}$	$c'_p = 1.7\ \mathrm{kJ\,kg^{-1}\,K^{-1}}$
Decomposition:	$Q'_d = 150\ \mathrm{kJ\,kg^{-1}}$	T_{D24} = 130 °C
Physical data:	Acetone	T_b = 56 °C

Assessment of the Energy Potential

- Potential
  - Reaction $$\Delta T_{ad} = \frac{Q'_{rx}}{c'_p} = 135\,K$$
  - Decomposition $$\Delta T_{ad} = \frac{Q'_d}{c'_p} = 89\,K$$
  - Overall $$\Delta T_{ad} = 224\,K : HIGH$$
  - Final temperature $$T_f = 264\,°C$$

Example Condensation Reaction

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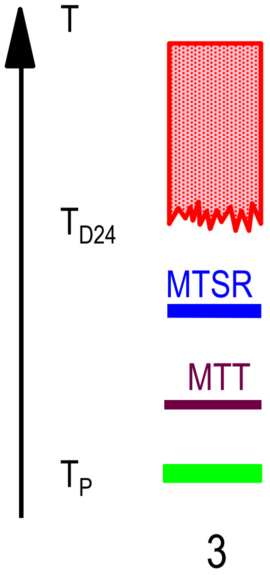
Physical data:	Acetone	T_b = 56 °C

Criticality Class

- T_p 40 °C
- MTSR 81 °C
- T_{D24} 130 °C
- MTT 56 °C
- Criticality class 3



MTSR Determination $T_p + X_{ac} \cdot \Delta T_{ad} = 81°C$

Example Condensation Reaction

Process Description

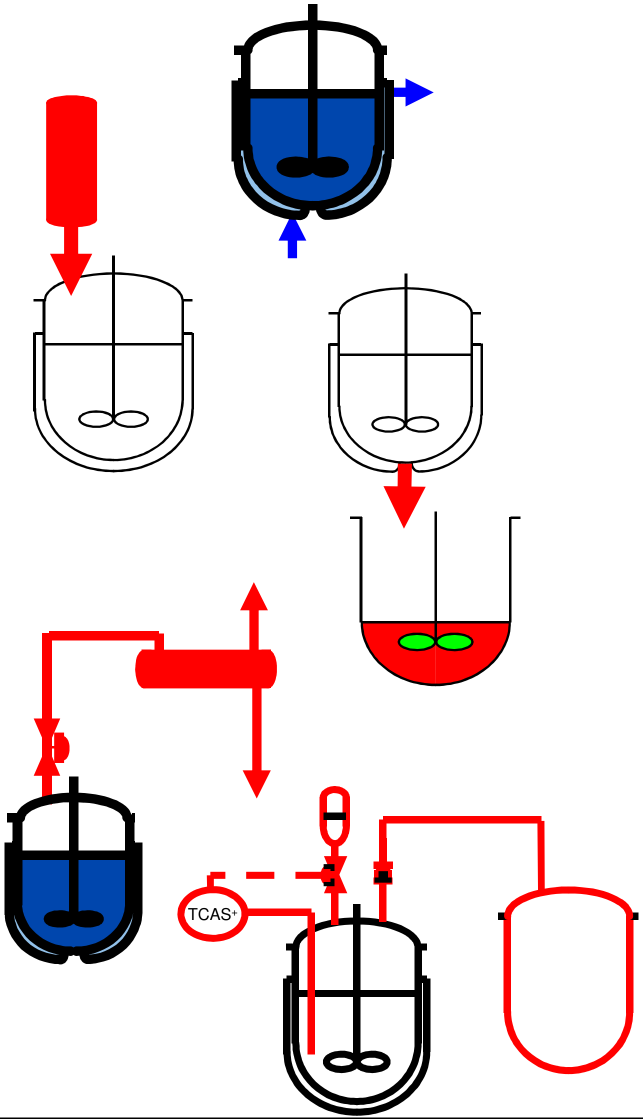
- Solvent: Acetone
- Charge: 2500 kg
- Reaction temperature: 40 °C.
- Semi-batch with stoichiometric addition in 2 hours
- Maximum accumulation is 30% (at end of addition).

- Heat release rate at end of addition: 20 W/kg
- Condenser power 250 kW
- Vapor tube DN250
- Physical data of Acetone

Mw	58 g/mol
Tb	56 °C
$\Delta_v H$	523 kJ/kg
LEL	1.6 % v/v

Vapor Release and Thermal Behavior at MTT

- Vapor released $$m_v = \frac{(MTSR - MTT) \cdot c_p' \cdot m_r}{\Delta H_v'} = 203 kg_{vap}$$
- Flammable cloud $$V_{ex} = \frac{m_v}{\rho_v \cdot LEL} = 5885\ m^3$$
- Power at MTT $$q'_{(MTT)} = q'_{rx} \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T_p} - \frac{1}{MTT}\right)\right] \cdot \frac{MTSR - MTT}{MTSR - T_p}$$ $$q_{(MTT)} = 200\ kW$$
- Vapor velocity $$u = \frac{q}{\Delta_v H} \cdot \frac{4}{\pi d^2} = 3.7\ m/s$$



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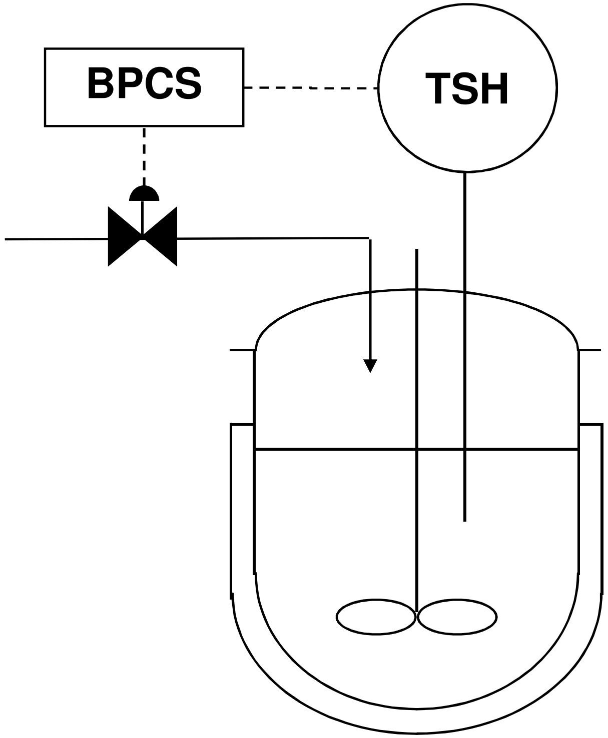
Example ERS Sizing

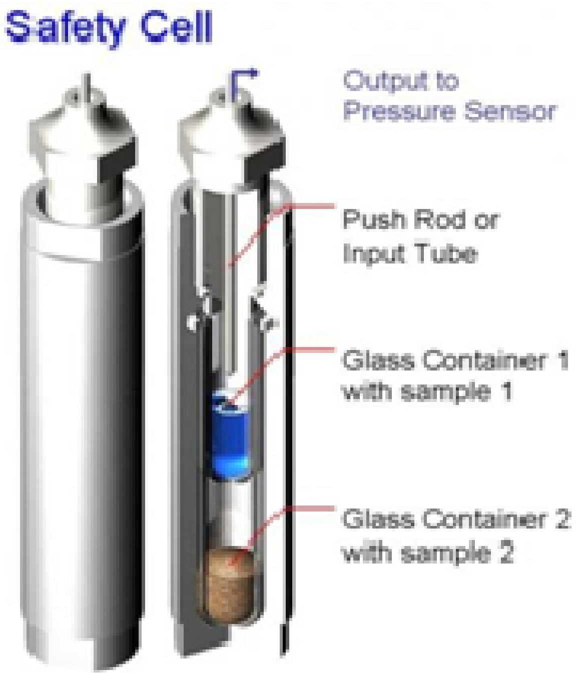


- Semi-batch reaction at 30 °C

- Problem:
  - What happens in case of feed failure: if feed is added in one shot?
  - Is pressure relief sizing sufficient

    P_{set} = 4 bar g ?

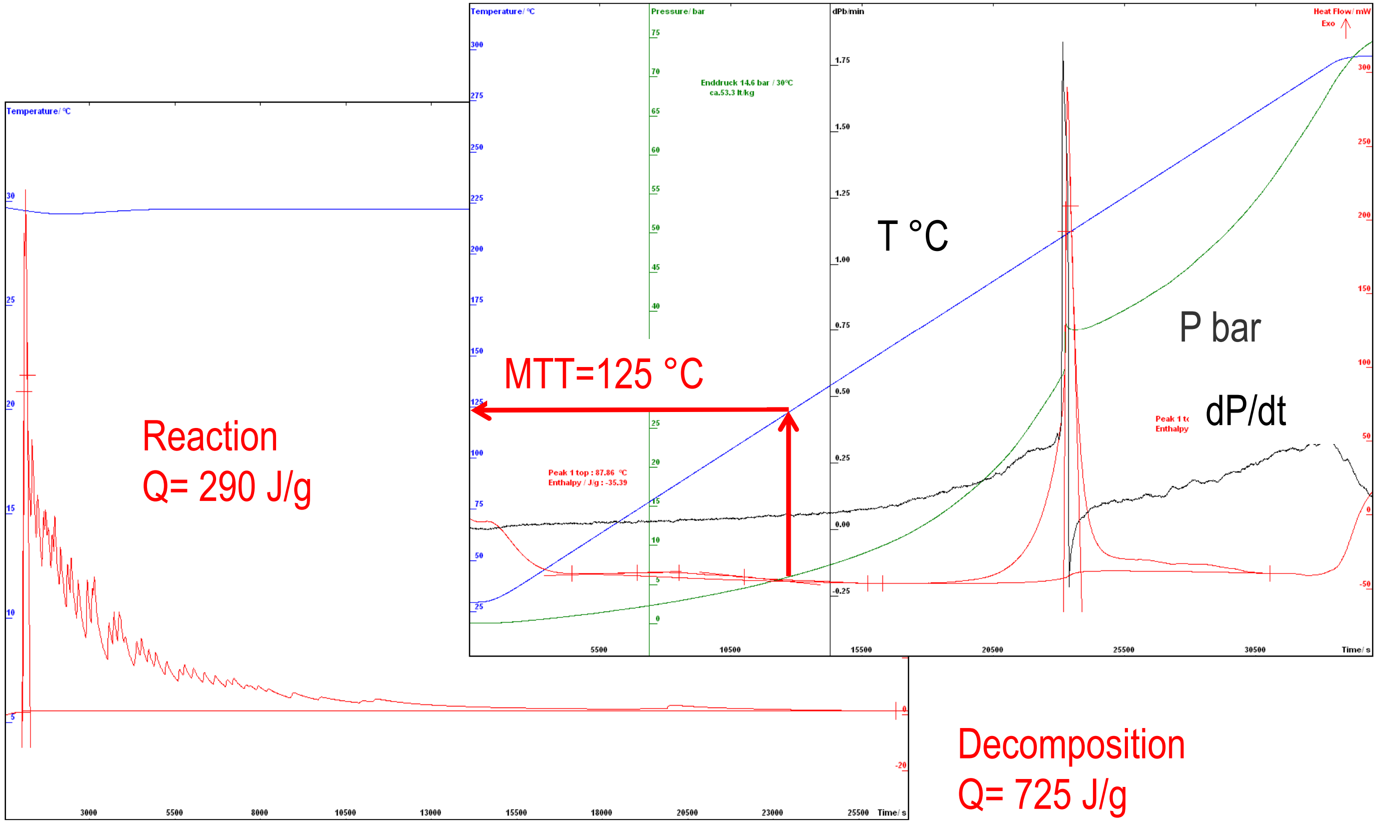
Calvet Calorimeter



Setaram C80

- Differential calorimeter
- Typical Sample mass 0.1 to 1 g
- T: 30 – 300 °C
- P: 0 - 200 bar
- With Safety cell

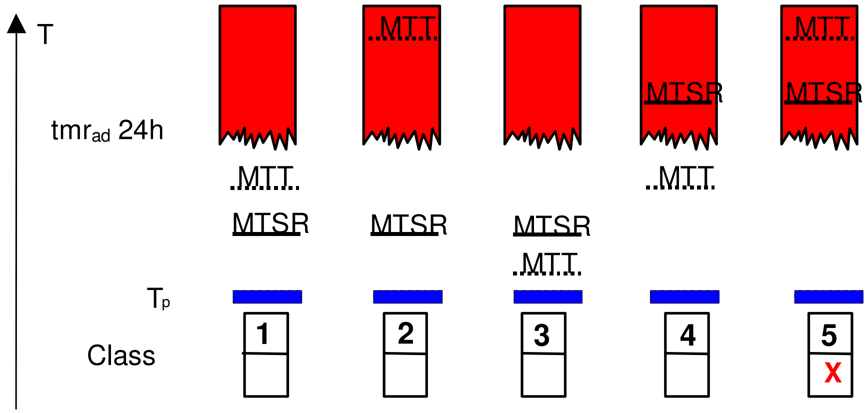
Experiment 1: Simulation of the Failure Scenario



- Isothermal test at 30 °C
- then heating to 300 °C

- Reaction ΔT_{ad} = 170 K
- MTSR = 200 °C
- MTT = 125 °C
- T_{D24} = 90 °C
- T_f = 626 °C
- q $_{reaction}$ with exponential decay
- Pressure with «explosive» increase

Assessment of Criticality and Protection Strategy



- MTSR = 200°C
- MTT = 125°C
- T_{D24} = 90°C
- T_p = 30 °C

Criticality Class 5 requires

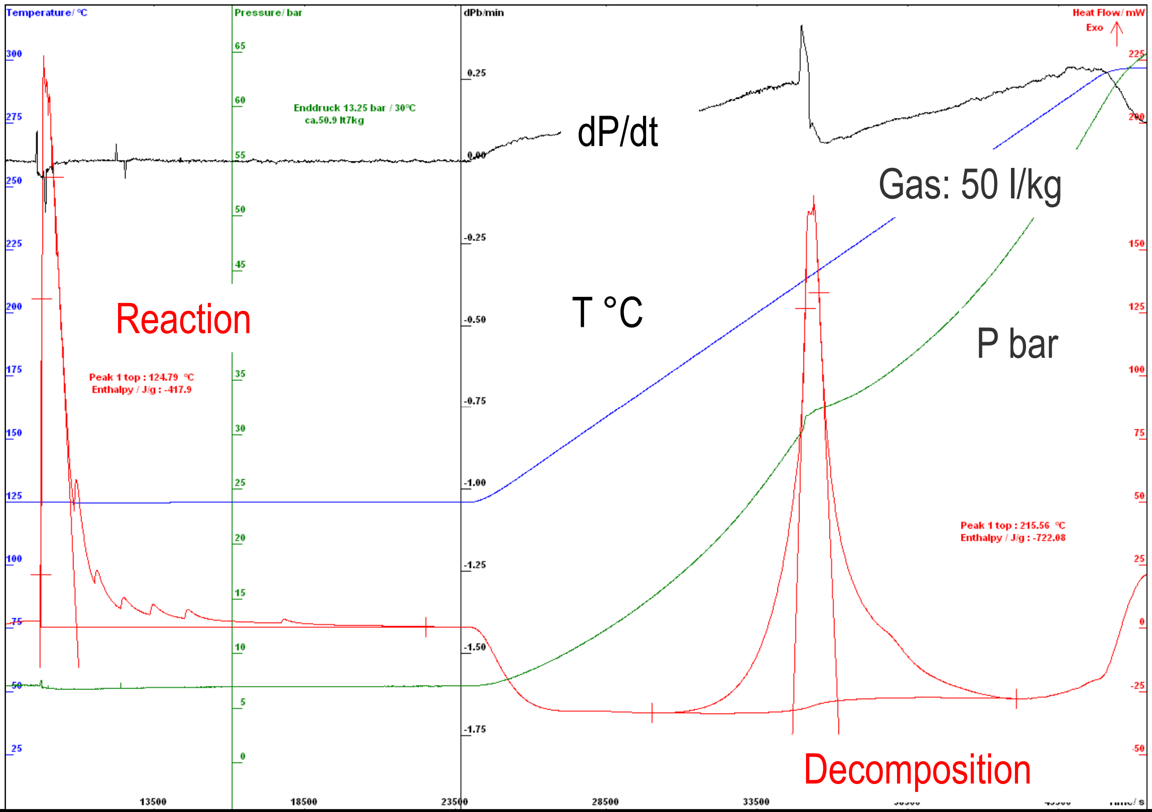
- Reworking of the process

or

- Emergency measures

- Recommendations
  - Avoid triggering the decomposition
  - Secure addition: limitation of flow rate
  - Pressure relief must take place during synthesis reaction

Experiment 2: Behavior at MTT

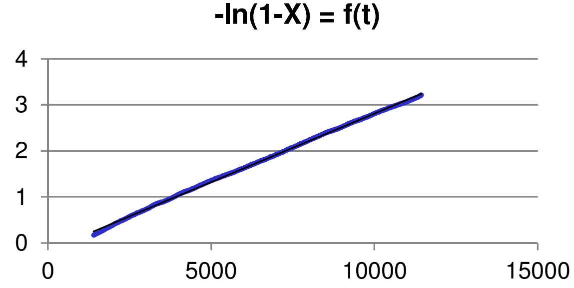


- Reaction at 125 °C (MTT)
- Thermal stability up to 300 °C
- ➢ Experimental decay confirmed
- ➢ Gas production 50 l/kg

ERS Design Data from Calvet Calorimeter

- Kinetic evaluation as 1st order
- Interpolation 30 – 125 °C
- Extrapolation to 137°C (MAWP)
- Use of vapour pressure data

Kinetics
First Order reaction
-ln(1-X) linear function of time
Activation energy from 2 temperatures



- Recommendations
  - Secure feed (interlock with T, orifice plate or C_{vs} Valve)
  - Choose set pressure as low as possible

Case	1	2
Device	SV	SV
P_{set} [bar g]	0.5	4.0
T_{set} [°C]	79	125
q [W/kg]	240	450
d [mm]	32 / 60	49 / 92

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Reliability of Protection Against Runaway

Based on Standard IEC 61511

Process Hazard Analysis

- Description of the scenario
- List of protection measures

alone gives no guarantee the required safety level is achieved

- Reliability analysis is required.

Required Risk Reduction

- Risk Matrix 6 x 4
- Risk reduction factors

Frequency			1	2	3	4
	A	f > 1/10 a	100	1000	10’000	100’000
	B	f ≤ 1/10 a	10	100	1000	10’000
	C	f ≤ 1/100 a		10	100	1000
	D	f ≤ 1/1000 a			10	100
	E	f ≤ 1/10’000 a				10
	F	f ≤ 1/100’000 a				
			Severity			

Accepted Risk no Measure Required

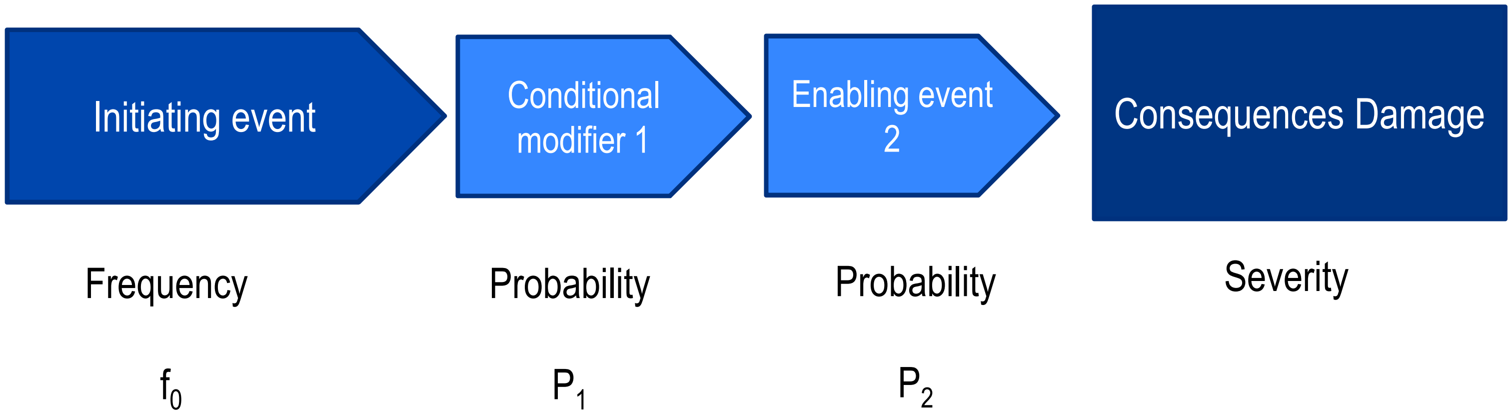
ALARP: As low as Reasonably Practicable

Unaccepted Risk Measure Required

Unaccepted Risk PCS measures insufficient

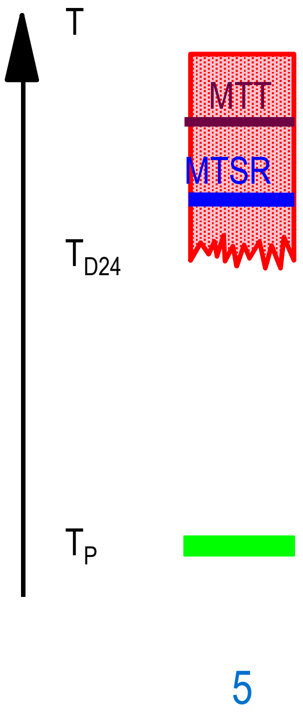
Structure of a Scenario (after LOPA)

- Independent events
- Only logical AND gates



$$f = f_0 \cdot \prod_i P_i$$

Example Structure of a Runaway Scenario

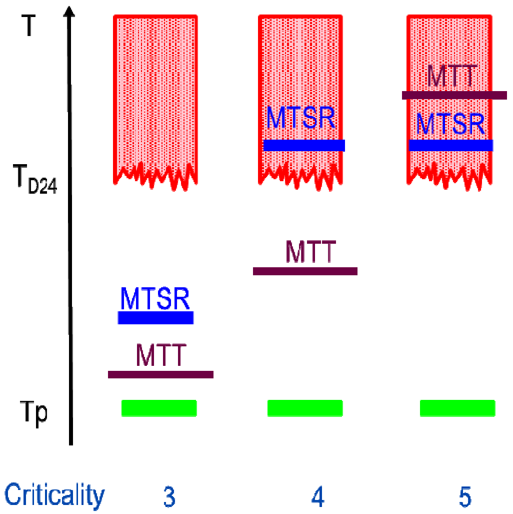


			Risk 1			Risk 2	
Id.	Causes	Hazard Consequences	S	F	Risk reducing measures	S	F
Cooling failure	Failure of cold water supply f_0= 1/1 y	If failure during last 2 hours of feed (P=20%) then Accumulation leads to high temperature and pressure above MAWP, LOC flammable vapor escaping, Explosion if Ignited (P=1/100), Operators present (P=1/1), Causing 1-2 fatalities	**4**	**C**	T/O: Emergency cooling using city water triggered by operator following TAH (1/1) T: Interlock: TSHH stops feed (1/10) T: PSV (1/100)	**4**	**E**

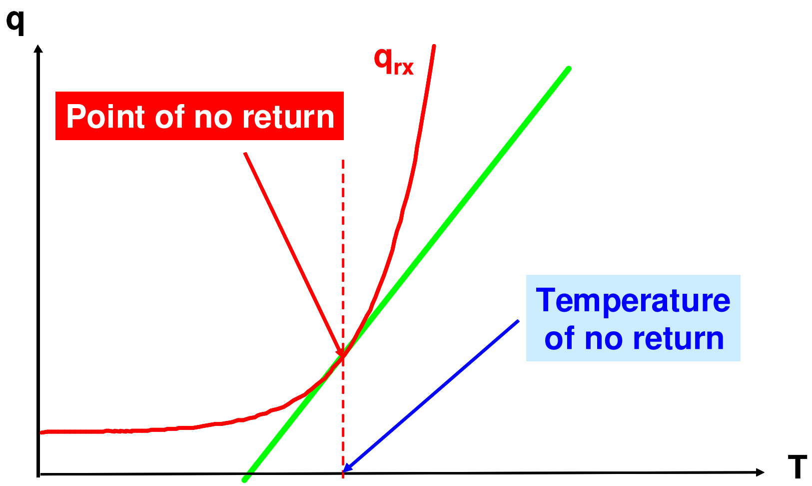
- Initiating event → Enabling event → Conditional modifiers → Consequences

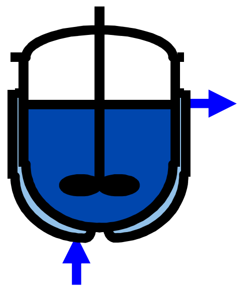
Emergency Cooling

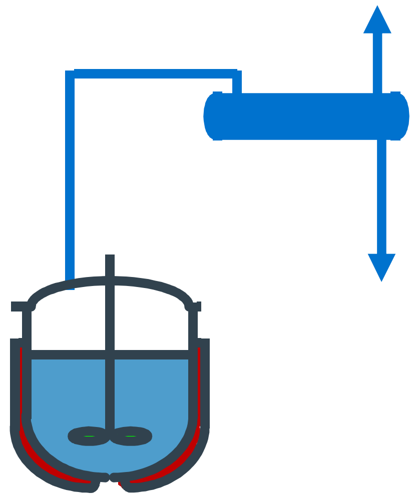
- Required Power from Calorimetry



- Must be independent of utilities
- Limitation in case of solidification
- Agitation is critical

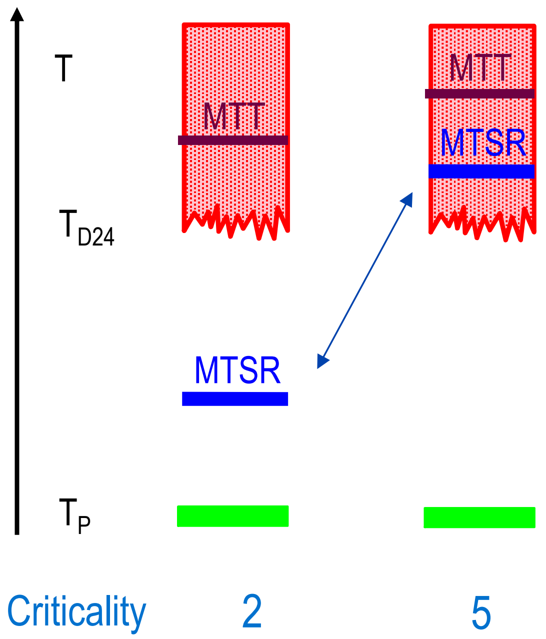






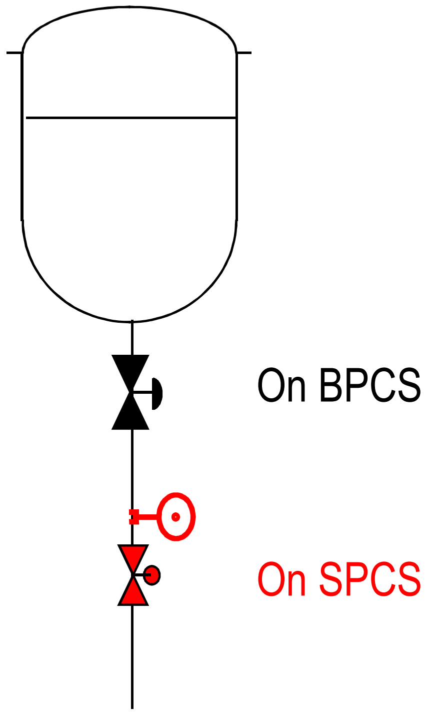
Feed in Semi-Batch Reactors

- The feed determines
  - the accumulation
  - the MTSR



Controlling the feed

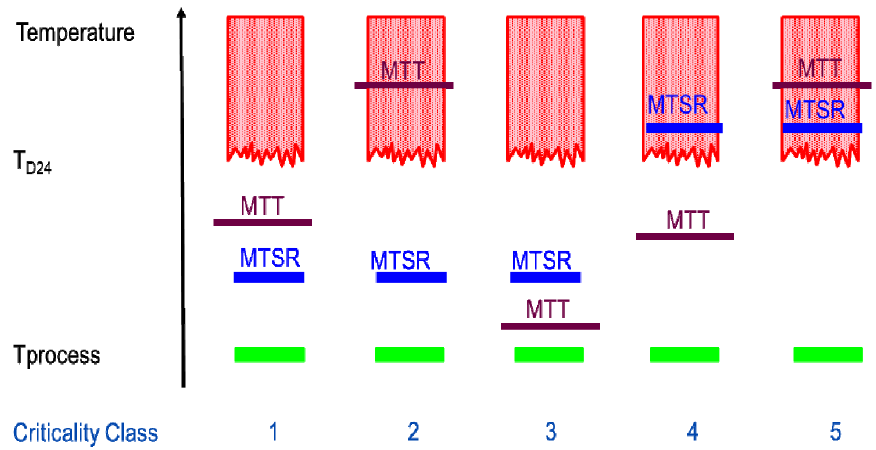
- Amount of feed
  - Portions
  - Redundant feed valves
- Feed rate
  - Orifice
  - Volumetric pump
- Stopping the feed
  - Interlock with Temperature + / -
  - Interlock with Stirrer



Conclusion

Criticality Classes for Runaway Hazards

- Simple language
- Scientific roots
- Strengthens the Systematics of the Risk Assessment
- Guide for Definition of a Protection Strategy
- Delivers the Thermal Data for the Design



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- Swiss Federal Institute of Technology (EPFL)

❖ PhD students

EPSC

EPSC
THE PROCESS SAFETY NETWORK

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❖ My wife for her patience

TÜV SÜD Process Safety
Mattenstrasse, 24a
CH-4002 Basel

Phone: +41 (0)58 517 80 20
Fax: +41 (0)58 517 80 21

Email: info.bs@tuev-sued.ch

CONTACT US

Process Safety